MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A

AFOSR-TR. 86-0849

SURFACE GENERATION OF ELECTRONICALLY EXCITED STATES OF O₂

Final Scientific Report

July 7, 1986

Prepared for:

U.S. AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
Bolling Air Force Base
Washington, D.C. 20332

AD-A172 426

DTIC FILE COPY

SRI Project No. PYU-4219
Contract No. F49620-82-K-0025
MP 86-130

SRI International
333 Ravenswood Avenue
Menlo Park, California 94025-3493
(415) 326-6200
TWX: 910-373-2046
Telex: 334 486

86 10

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
Unclassified	

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT
N/A	Approved for public release; distribution unlimited.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
N/A	

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
MP 86-130	AFOSR.TR. 86-0849

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
SRI International		Air Force Office of Scientific Research

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
333 Ravenswood Ave. Menlo Park, CA 94025	Bolling Air Force Base Washington, DC 20332

8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
AFOSR	NC	F49620-82-K-0025

9c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
Bolling Air Force Base Washington, DC 20332	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO
	61102F	2303	A2	

11. TITLE (Include Security Classification)

SURFACE GENERATION OF ELECTRONICALLY EXCITED STATES OF O_2

12. PERSONAL AUTHOR(S)
Tom G. Slanger

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final	FROM _____ TO _____	86-07-09	vii + 54

16. SUPPLEMENTARY NOTATION

17	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

This investigation of surface-related processes consisted of two parts; laboratory studies of the production and loss of electronically excited oxygen species on metallic surfaces, and an investigation of the mechanisms that might contribute to the so-called Space Shuttle glow. In the laboratory work, production by atom recombination of the states of O_2 that lie between 4 and 5 eV was studied. The efficiency of their generation was correlated with the identity of the metal, its position on the periodic chart, surface temperatures, alloy composition, and the electronic heat capacity. Spectra of the emissions originating at the surfaces were shown to be non-specific to the particular metal, implying that internal energy distributions in the emitting metastable molecules were determined by gas phase interactions. Further study of surface energy accommodation, and the possible generation

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS	
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL
		NC

DD FORM 1473, 84 MAR   83 APR edition may be used until exhausted.   SECURITY CLASSIFICATION OF THIS PAGE
All other editions are obsolete.

of highly vibrationally excited molecules is called for. The loss of $O_2(a^1\Delta_g)$ on metallic surfaces was investigated, and showed both similarities and differences with the production of the higher O_2^* states on the same surfaces. Metals in a given group of the periodic chart tend to exhibit similar temperature effects.

The Space Shuttle glow study involved development of a model for the process, which has been useful in guiding the investigations as subsequent in situ experiments have been carried out. By consideration of the present status of the observations, it has been found possible to clarify which of the current explanations of the glow-forming mechanism are viable, and which must be discarded.

SURFACE GENERATION OF ELECTRONICALLY EXCITED STATES OF O₂

QUALITY INSPECTED 4

Accession For	
NTIS GRA&I	☒
DTIC TAB	☑
Unannounced	☐
Justification	

Final Scientific Report

July 7, 1986

By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

By: Tom G. Slanger

Prepared for:

U.S. AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
Bolling Air Force Base
Washington, D.C. 20332

SRI Project No. PYU-4219
Contract No. F49620-82-K-0025
MP 86-130

Approved by:

Donald C. Lorents

Donald C. Lorents, Laboratory Director
Chemical Physics Laboratory

G. R. Abrahamson
Vice President
Physical Sciences Division

SRI International

SUMMARY

This project focus on the interactions of atoms and excited molecules with surfaces. The objectives of the program were (1) to elucidate the mechanism of the so-called Space Shuttle glow and 2) to conduct a laboratory study of oxygen atom recombination and excited oxygen molecule destruction on metal surfaces.

In two papers published on the Space Shuttle glow problem, arguments were presented concerning the identity of the emitting species on shuttle surfaces as well as those of other space vehicles. Several mechanisms of glow production were suggested based on existing photographic data, and various hypotheses involving plasma discharges, gas phase excitation effects, and glow excitation by thermal particle collisions were judged to be invalid.

In the laboratory study, two processes were investigated. In the first, the metastable 4-5 eV states of O_2 were generated on various metallic surfaces by the recombination of atoms produced in a microwave discharge. The relative efficiencies of production of the resultant UV glows were measured, their behavior as a function of temperature was studied over the temperature range 210-520 K, the glow spectra emanating from the surfaces were compared, glow intensities were related to composition for a series of nickel alloys, and correlations were made with various physical properties of the surfaces. One of the more important recommendations is that further work is necessary to determine the dominant pathway by which large fractions of the recombination energy are taken from the surfaces by the newly formed molecules.

In the second laboratory study, the loss of $O_2(a^1\Delta_g)$ on metallic surfaces was investigated. A considerable range of activities was measured, and the results of thermal measurements plotted as loss <u>vs</u> temperature profiles showed significant variations. Metals with similar chemical properties tended to produce similar profiles, both in the $O_2(a)$ loss measurements and in excited molecule production. Different surfaces were investigated by Auger spectroscopy to establish to what extent the data relate to a metallic, rather than an oxide, environment.

CONTENTS

ILLUSTRATIONS

TABLES

I INTRODUCTION

The interactions of radicals and atoms with surfaces is a topic that is drawing increasing attention. Not only are questions of heterogeneous interactions of intrinsic interest, but there are also practical reasons for attempting to understand the various phenomena. Perhaps one of the more dramatic examples is the issue of spacecraft glow, exemplified by the now well-documented Space Shuttle glow.[1-5]

The project described here focused on two surface-related studies. First, laboratory experiments were performed to investigate the recombination of oxygen atoms on surfaces. Topics investigated included the generation and destruction of electronically excited states, the temperature effects for such processes, and the efficiency for these interactions on various surfaces, principally metallic. Second, we attempted to integrate the various observations regarding spacecraft glows into a coherent pattern and to develop a hypothesis to explain the mechanisms of glow production.

Although innumerable studies have been performed on the energy transfer between surfaces and free or adsorbed molecules, relatively few have examined electronically excited states, and fewer still have investigated such states that are metastable with respect to radiation. Metastability is not necessarily a desirable feature in such investigations, but to study the interesting case of oxygen atoms and molecules on surfaces, one is faced with the fact that transitions between the six lowest O_2 states are all forbidden to one degree or another.

The early work on excited state generation by means of oxygen atom recombination on surfaces was performed by Harteck and co-workers[6-8] 20 to 30 years ago; relatively little research has been carried out in the interim. One of the attractive features of such measurements is that there is a considerable intensity enhancement over homogeneous recombination glows, so the possibility exists of obtaining kinetics and spectroscopy measurements that are otherwise difficult or impossible. For example, Ogryzlo and co-workers[9-11] have taken advantage of this effect.

1

The $O_2(a^1\Delta_g)$ state, generically known as singlet oxygen, is a very important entity for several reasons. Although rather unreactive compared to other excited states (its excitation energy is only 1 eV), it is nevertheless much more reactive than ground state O_2. Coupling its stability with its extremely long radiative lifetime (4×10^3 s) makes it possible to transport it from its point of production in a way that is unique among electronically excited molecules. This property is used to good advantage in the $O_2(a)/I^*$ laser and was one of the reasons for AFOSR's interest in the current work. Singlet oxygen is also a useful molecule in medical applications as an agent for treating certain cancers, being generated in situ by a photosensitization process.

The phenomenon of the Space Shuttle Glow has attracted worldwide interest since it was first discovered in 1982. The red-orange glow is observed around surfaces of space vehicles in orbit and is a consequence of the 8 km/s orbital velocity, which defines the interaction energy with which a particle collides with these surfaces. Apart from the glow, the collisional energies (5 eV for oxygen atoms) of the particles are sufficient to cause damage and erosion. Because the glow is a manifestation of these processes, it is of importance in reaching an understanding of the relevant mechanisms.

II RESULTS

A. Spacecraft Glows

The phenomenology of spacecraft glows is, in retrospect, a long-standing issue. Twenty years ago there were reports of Russian rocket missions in which surface-related radiation was described,[12] but apparently there was a general disbelief in Western scientific circles, and the subject was not pursued, in spite of sporadic literature reports of similar observations. It was not until data from the Atmospheric Explorer satellite in 1977 indicated the presence of surface glow phenomena that the subject was taken seriously.[13] Since then and particularly with the start of Space Shuttle missions, interest in these glows has rapidly increased.

An understanding of the nature of surface glows on orbiting and reentry vehicles is of considerable importance for two principal reasons: interference and detection problems. During scientific optical experiments, the spacecraft glow can interfere with observations because atmospheric and astrophysical measurements can obviously be affected by the presence of a near-field glow. As a result of this pheomenon, planners have re-evaluated the proposed orbital altitude of the Space Telescope.

From a military standpoint, the question of detectability of space vehicles is of great interest. For both offensive and defensive forces, it is clearly advantageous to be able to detect and monitor satellites, rockets, and missiles by their optical signatures, and understanding the processes involved is the first step toward learning how they can be controlled.

Since the first shuttle glow reports three years ago, researchers have tried to understand the nature and the source(s) of the glow. Among the reported characteristics of these vehicle glows are that the intensity follows the ambient density of oxygen atoms,[4] that the glow is strongest on surfaces perpendicular to and facing the direction of motion of the vehicle,[4] that the color is red-orange,[3] and that the glow extends, at least on the shuttle, 20 cm from the surface.[3] The initial reports, based on indications that oxygen atoms seemed to be necessary for glow generation, suggested that the

emitter was an excited O_2 molecule. This idea was rapidly rejected following the realization that the radiative lifetime of any of the relevant O_2 states was much too long to produce a glow with a thickness of only 20 cm.

At this point, we suggested that the glow on the Atmospheric Explorer was consistent with the emitter being vibrationally excited ground state OH, the Meinel system.[5] The following arguments favored such an identification: (1) The apparent glow thickness, substantially larger than on the Shuttle, could be interpreted, on the assumption of thermal ejection velocities of the emitting molecule, as arising from a 5-ms radiator (the OH radiative lifetime from high vibrational levels has this value). (2) It is possible that the interaction of the fast (8 km/s) oxygen atoms with surfaces can generate OH because contamination by water and hydrocarbon materials is expected. (3) The distribution of radiation, peaking toward the infrared, is representative of the Meinel system, which is most intense in the 1-2 μm region. Appendix A is a reprint of the paper published in Geophysical Research Letters on this topic.

Two subsequent experiments lent support to the OH hypothesis. A ground-based measurement of a Shuttle overflight[14] indicated strong infrared emission at 1.6 and 2.3 μm, and a Fabry-Perot interferometric experiment[15] on the Dynamics Explorer satellite showed spectral lines in the correct positions for the OH identification.

Although initial attempts to measure the spectral distribution of the glow from the shuttle were inconclusive, within the last year it has become apparent that in the visible spectral region, the radiation is essentially continuous.[16] The present resolution of 3.4 nm is sufficient to show structure in OH and in any of the emissions proposed more recently, such as NO[17] and N_2.[18] Thus, it appears that for the shuttle, the predominant <u>visible</u> radiation is not from any of these species. Such a conclusion certainly presents ambiguities, and there is still much work to be done in resolving the issues.

From their most recent Shuttle measurements, Swenson et al.[16] have argued that the most likely emitting molecule is NO_2, basing this conclusion on the fact that the only small-molecule continuum of which we are aware that
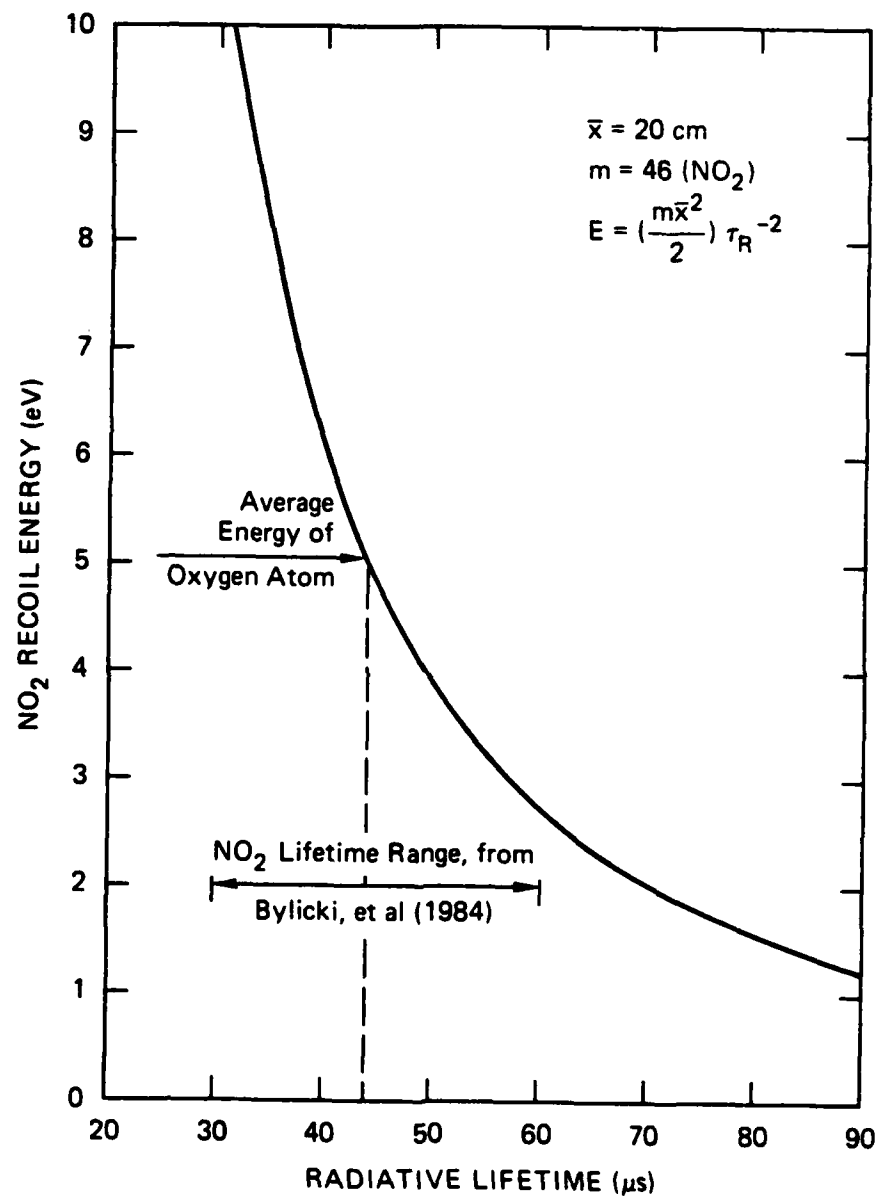
approximates the appearance of the observed spectrum is that from NO_2. They propose that its source is surface collection of individual ambient O and N atoms.

Although the Shuttle continuum is narrower than the continuum from $O + NO$,[16] the most questionable part of the NO_2 identification is that the thickness of the glowing region has always been taken as an indication that the emitter cannot be radiating in an optically allowed transition. For example, an air molecule (O_2, N_2, NO) with a 1-μs radiative lifetime, leaving a surface with a 300 K thermal velocity, will travel only 0.4 mm before emitting a photon. Thus, a 20-cm thickness indicates either that the emitter is a metastable molecule or that the recoil velocity is very high and bears no relationship to the surface temperature.

Assuming that the shuttle emitter is indeed NO_2 and that the distance travelled before photon emission is 20 cm, the relationship between the energy of the departing molecule and its radiative lifetime can be calculated as shown in Figure 1. This figure shows that if the lifetime is longer than 100 μs, then not much suprathermal energy is needed, but if the lifetime is within the 30-60 μs range measured recently by Bylicki et al.,[19] the equivalent energy range is 3-12 eV. Because the available translational energy in incoming oxygen atoms is 5 eV, such an amount of energy in departing NO_2 is unrealistic and unprecedented. Unfortunately, it is not possible to definitively discount NO_2 as the emitter because a considerable range of radiative lifetime values are available in the literature,[20-23] some exceeding 100 μs. The complexity of the interactions between the NO_2 states responsible for the continuum emission is such that it is difficult to choose "correct" lifetime values, and it is particularly difficult to reach conclusions about the detailed quantum states of NO_2 molecules that might arise from surface reactions. It is clear that considerably more study is required before these issues will be sufficiently clarified to make further progress possible. Many more observational data are needed from the shuttles and satellites, and it is also important to perform laboratory simulations, particularly as a means of verifying hypotheses developed from the in situ observations.

Our initial interest in spacecraft glows centered on the identification of the emitting species, but an intimately related question has to do with the mechanism of the process generating excited molecules. Several possible

RECOIL TRANSLATIONAL ENERGY VERSUS RADIATIVE LIFETIME

$\bar{x} = 20$ cm

$m = 46$ (NO_2)

$E = (\dfrac{m\bar{x}^2}{2})\, \tau_R^{-2}$

Average Energy of Oxygen Atom

NO_2 Lifetime Range, from Bylicki, et al (1984)

NO₂ RECOIL ENERGY (eV)

RADIATIVE LIFETIME (µs)

JA-330543-119

FIGURE 1

6

mechanisms have been suggested, and some aspects of these can be discussed without knowing the emitter identity. Appendix B is a copy of a paper that has appeared in Geophysical Research Letters that deals with these issues, and its premise is that existing photographs of the glow on the Shuttle set restraints on proposed generation mechanisms. It has been suggested that excited species can be produced in the density-enhanced regions near forward-facing surfaces by gas phase collisions of incoming fast particles with the particles in this skin region. Alternatively, Papadopoulos has proposed[24] that a plasma can develop near the surface, and excitation by electrons or ions could then occur. From the photographs,[25] it is apparent that gas phase excitation processes are excluded as major sources of the glow, leading one back to the original concept that the excited species are created at the sur-face by fast particle interactions. It also appears that if any incoming par-ticles reflect from the surfaces, they have lost sufficient kinetic energy to lie below the threshold for surface excitation.

B. Laboratory Surface Studies

1. Surface Recombination of Oxygen Atoms

The recombination of ground state oxygen atoms into the six molecular states shown in Figure 2 is a subject whose complexity has not been fully appreciated. It is becoming evident from recent experiments that we do not yet understand the details of the process even in the gas phase. In partic-ular, the branching ratios into the individual states have not been measured, we do not understand how or whether the states are collisionally coupled, and we are uncertain about the kinetics of the relaxation from the nascent mole-cule to the bottom of the potential in any state. Also, recent studies[26-29] refer to precursor species in the kinetic scheme, another indication that the flow of energy is not understood.

In many ways the oxygen atmospheric nightglow is the best medium in which to study atom recombination, because the pressure domain cannot be duplicated in the laboratory. That is, the six O_2 molecular states are such poor radi-ators that at low pressures deactivation on vessel walls dominates the loss process, and no emission is observed. On the other hand, in the nightglow no such effect occurs, and the efficiency of radiation is much greater. Never-theless, attempts to model the system and to explain appearance

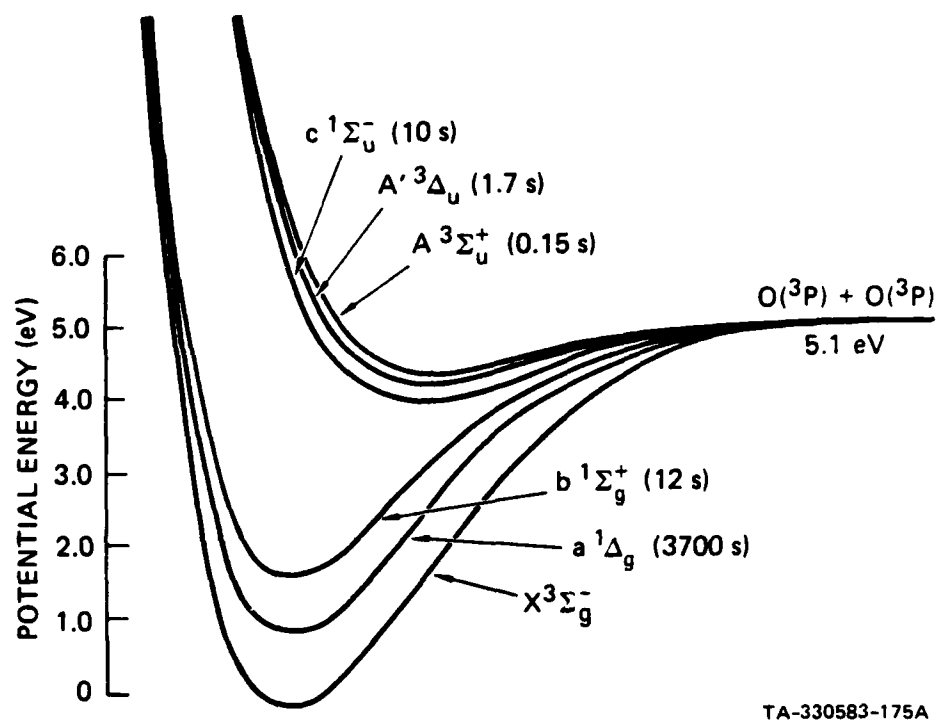# OXYGEN MOLECULAR ENERGY LEVEL DIAGRAM

FIGURE 2

TA-330583-175A

8

of species such as $O(^1S)$ have paralleled the laboratory studies,[26,29] and similar discussions of precursor involvement are taking place.

Oxygen recombination on surfaces has been studied much less, and what data exist are generally of a phenomenological nature. Work in this area was begun by Harteck and co-workers[6-8] in the late 1950s and was basically limited to observing that when oxygen atoms recombine on various metallic surfaces, production of $O_2(A^3\Sigma_u^+)$ is observed; this process is most efficient for nickel surfaces although cobalt behaves in a similar manner. More recently, this effect has been used by Ogryzlo and co-workers[9-11] to generate excited O_2 states, specifically $A^3\Sigma_u^+$ and $c^1\Sigma_u^-$, for kinetics studies.

We investigated surface recombination to learn more about the interaction of electronically excited oxygen molecules with surfaces. The fact that oxygen atom interactions with the Space Shuttle seems to be related to the observed glow was coincidental, although we rapidly found ourselves part of the community investigating these effects.

The early work of Harteck and co-workers[6-8] was limited to production of the $O_2(A)$ state. However, we observed that recombination of oxygen atoms on Pyrex surfaces led to a high yield for production of $O_2(a^1\Delta_g)$,[30] the lowest excited O_2 state and the driving force in the iodine laser. The Air Force was interested in how this state was generated on other surfaces because, although the yield on Pyrex is 35%, the efficiency is low, the probability per collision of an oxygen atom recombining on the surface being about 10^{-4}.

Ongoing work at SRI on the 4-5 eV states of O_2[31-33] has been instrumental in demonstrating that, although the $O_2(A)$ state is the best radiator ($\tau \sim 150$ ms), the concentrations of the c and A' states, with much longer lifetimes, are considerably greater, both in afterglow systems and in the nightglow. Thus, in all studies performed to date, including those of Harteck et al.,[6-8] it must be remembered that reports of emission arising predominantly from $O_2(A)$ are misleading to the extent that it is not the dominant excited species of the higher states. Nevertheless, it is not a simple matter to study the c and A' states individually, precisely because the A state produces most of the light in the spectral region where extraneous emissions are minimized, 300-400 nm. As a result, although we have obtained spectra showing all three states to be present from surface recombination, the photometric measurements on the efficiency of production of these excited states on surfaces refer

9

mainly to the A state. As pointed out earlier, it is not clear how the three states are collisionally coupled, that is, whether O_2 or He collisions convert one state into the other. If such processes occur, then it may be immaterial which state is monitored.

In the next section we describe the experiments performed on generation of the 4-5 eV states on a variety of surfaces, relating atom losses to relative production efficiencies and determining the effect of temperature variations for several of the surfaces.

A philosophical point decided on early in the program was that no attempt would be made to use ultraclean high vacuum techniques. Because of the poor radiative efficiency of the O_2 states, we realized that it was necessary to work with relatively high concentrations of atoms. This precluded any low pressure sources such as atomic beams, constraining us to using discharge sources that operate at pressures in the 0.1-1 tor⁻ range. Thus, any type of surface treatment to ensure cleanliness or to ensure that the actual surface was the metal under study was futile. We had to accept that we were studying surfaces that were oxidized to some extent and that the physical properties of these surfaces were not well defined.

2. Surface Generation of 4-5 eV Oxygen States

To observe emission from surface-generated O_2 in the A, A', and c states, we described and built the apparatus shown in Figure 3. With this system, we were able to obtain measurements not only on the 4-5 eV states, but also on the loss rates of the $a^1\Delta_g$ state, described later.

Atoms were produced by a microwave discharge upstream of the sample region. After considerable experimentation, the most satisfactory feed gas was found to be a low pressure (500 mtorr) of pure O_2. This combination gave a higher absolute atom production than either higher O_2 concentrations or NO-titrated N atom flows. With the latter, the samples were sometimes poisoned, if excess NO was inadvertently used, and in any case there was always a control problem in keeping the flow at the titration point, where both N and NO were minimal.

To determine efficiencies of excited O_2 (O_2^*) production, it was necessary to measure not only the emission intensities, but the loss of oxygen

10

Adjustable
Feedthrough
with Temperature
Control

Sample

NO, NO$_2$

NO$_2$

To 50 cfm
Pump

Micro
Wave
Cavity

Phototube

Gas Input

N$_2$
O$_2$
He
Ar

H$_2$
Lamp

Vacuum
Monochromator
and Detector
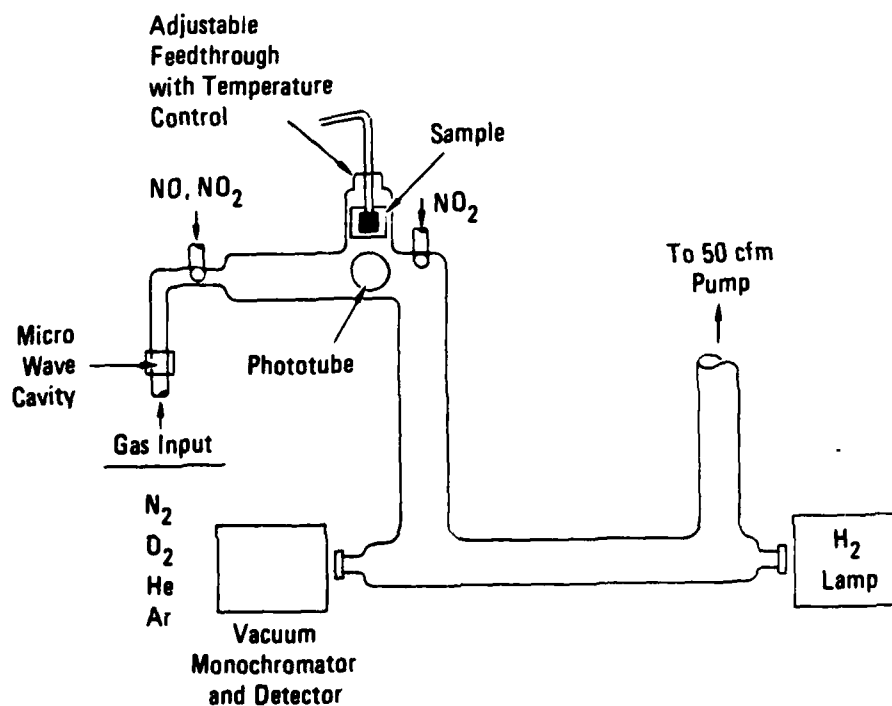
RA-330522-11

FIGURE 3

APPARATUS FOR OBSERVING EMISSION FROM SURFACE-GENERATED O$_2$ IN A, A', AND C

atoms. Obviously, if oxygen atoms are not being lost in passing over the surfaces, the lack of emission says nothing about the efficiency of O_2 generation in excited states. Thus, atoms were measured before and after the sample region, by NO_2 titration, to obtain an estimate of the recombination rate. This was done both in the presence and the absence of samples, because some atoms are lost on the glass walls themselves.

The sample holder was constructed with the option of mounting samples on either one side or both. In the former case, an inert metal such as aluminum was used on the other side. Included in the body of the holder was a metallic U-tube that permitted circulation of hot oil and cold ethylene glycol to control the surface temperature, which was measured with a thermocouple.

Surface glows were measured with a filtered photomultiplier tube, sensitive to radiation between 300 and 400 nm. Observations were made normal to the sample surface, so that the issue of emitter lifetime did not have to be addressed.

One of the principal problems with the experiment was equilibration times. Often, several hours were required for the glow from a new sample to adjust to a final value, and this effect did not appear to be related to the atom recombination rate, but to changes with time of the O_2^*/O_2 production ratio. Care was taken when changing samples to keep the system purged with He or N_2, which was beneficial, and samples were stored under inert gas when they were not mounted. Nevertheless, in spite of these precautions, when a new sample was mounted, the O_2^* production efficiency tended to change over substantial periods of time. Although oxygen atom flow over the surface was an important factor in stabilizing the O_2^* production efficiency, time alone seemed to have a similar although weaker effect; that is, a sample that had been in the system over a weekend exhibited greater O_2^* production efficiency than when it was first mounted. Because of this behavior, it was never possible to compare more than two samples per day. Examples of the rate of the equilibration process are shown in Table 1 for Ni and Pt. Ni samples generally showed an initially high glow intensity, which decreased with time, whereas Pt showed the opposite behavior. The runs in Table 1 were carried out before the system was temperature-controlled; at least part of the fall-off in intensity of the Ni surface was due to increasing temperature. In a later

12

Table 1

Equilibration Times for Nickel and Platinum Surfaces

Times (Minutes)	UV Intensity (Normalized to Peak)	
	Ni	Pt
0	8	10
1	10	51
2	26	67
3	80	80
5	100	92
7.5	96	97
10	92	98
12.5	85	99
15	79	99
17.5	75	99
20	70	100
25	63	100
30	59	100
35	55	
40	52	
45	49	
50	47	
55	45	
60	44	

section, we show that for most surfaces the UV glow intensity decreases with both an increase and a decrease in temperature.

As mentioned above, the samples were sensitive to surface poisoning; passage of NO_2 over a strongly-glowing sample for a few seconds quenched the emission, and the surface did not recover from this treatment for days, in spite of continuous oxygen atom flow. Similar behavior was noted when N-atom flows that were over-titrated with NO were used. Obviously, some material becomes bound to the surface very strongly, and we are unable to say whether it is an impurity in these gases or whether there is formation of metallic nitrides, which could be impervious to O-atom attack.

Twenty-two metals were investigated, a large fraction of the metallic elements. The results of these 300 K measurements, listed in Table 2, show that, compared to the five active metals, all others are basically inert. The work of Reeves et al.[6] had established that nickel and to some extent cobalt were efficient surfaces. Kenner and Ogryzlo[9-11] have used Ni for similar experiments, but found Co to be inactive, whereas our results show that Pd, Pt, and Au are active in addition to Ni and Co.

The position of these five metals on the periodic chart is particularly striking because they are not randomly scattered but form a coherent contiguous group. All but Au are in the VIIIb group, whereas Au lies next to Pt. Other VIIIb group members, such as rhodium and iridium, are inactive, and silver, which adjoins both palladium and gold, reacts efficiently with oxygen atoms, producing no emission.

We have naturally been searching for a common denominator among these metals or their oxides that explains their uniqueness. They are generally good catalysts, forming strong bonds with oxygen atoms, but such a correlation is somewhat self-defeating as an explanation, because the more strongly bonded an atom is to the surface, the less likely it is to recombine with a labile atom to give high electronically excited states.

In considering the fact that several of the metals have low energy accommodation coefficients, we thought it important to consider their heat capacities. In so doing, we discovered that, although there is no correlation to the Debye temperature, there is a term in the low temperature heat capacity expression that is due to free electrons. This parameter, ϵ, is listed in

Table 2

320-380 nm GLOWS ON METALS AT 300 K

Metal	Intensity (nA)	Oxygen Atom Loss (mtorr)	Efficiency (Intensity/Loss) Ni = 100
Ni	350	0.3	100
Pt	60	0.2	26
Co	30	0.4	6.4
Au	22	0.4	4.7
Pd	30	0.6	4.3
Fe	7	0.6	1.0
Cr	0.5	0	-
Rh	0.3	-	-
Ir	0.1	-	-
Al	0	0.1	0
Cu	0	0.7	0
Ag	0	0.6	0
Sn	0	0.1	0
Zn	0	0	-
Ta	0	0	-
Mo	0	0	-
Zr	0	-	-
Er	0	0.1	0
Dy	3	-	-
Gd	0	0.2	0
Sc	2.5	-	-
W	0	0.5	0

Table 3, where the effective glow-producing metals are compared with those from which no glow was produced,[34] in spite of a discernible loss of oxygen atoms (those for which no atoms were lost are not included). The correlation is remarkable in that, except for gold, there is no overlap between the two sets; the lowest ϵ in the glow-producers is larger than the highest ϵ among the nonglowing metals. Excluding gold, the average ϵ is 5.5 times larger for the former than the latter.

On the basis of these observations, we predict that substantial glows might be observed from untested metals with high values of ϵ. The highest have been reported for lanthanum, manganese, scandium, uranium, yttrium, and vanadium. In fact, we did examine scandium, but it is not shown in Table 3 because, although a faint glow was observed, the oxygen atom loss was indiscernibly small. The same is true for dysprosium, for which a value for γ is not available. Thus, these may well be very efficient glow-producers, defining efficiency as glow intensity/atoms lost.

The definition of the electronic heat capacity is

$$C_v(el) = \epsilon T \tag{1}$$

$$\epsilon = \pi^2 zR/2T_f \tag{2}$$

where z is the number of valence or conduction electrons per atom and T_f is the Fermi temperature, approximately 5×10^4 K. The expression is reasonably valid for various metals, but there are many for which the value of ϵ is much larger than calculated, including the transition elements. The discrepancy is treated by multiplying ϵ by m^*/m, the "effective electronic mass," which has a value within a factor of 2 of unity for the metals that we find to be ineffective glow producers, but attains values up to 28 (for Ni and Pd) for those metals that generate glow. The concept of the effective electronic mass is used extensively in various areas of solid state physics, including magnetic susceptibility (paramagnetic metals have high values of m^*/m), transport of charge in semiconductors (for which m^*/m tends to be less than unity), and cyclotron resonance studies.

It is obvious that more work is needed to understand the apparent correlation between glow efficiency and m^*/m. We presume that it is not a primary

16

Table 3

ELECTRONIC HEAT CAPACITY FOR THE MOST AND
LEAST EFFECTIVE METALS IN GENERATING UV GLOWS[a]

Metal	$\epsilon \times 10^4$ (cal/mole-deg^2)
Most Effective	
Ni	7.1
Pt	6.8
Co	4.7
Au	0.7
Pd	9.4
Fe	5.0
Least Effective	
Al	1.4
Cu	0.7
Ag	0.7
Sn	1.8
W	1.3

[a]Source: Reference 34

effect, but that there is some physical or chemical parameter that is common to both phenomena. Since the transition metals seem to be characterized by large m^*/m ratios, whereas there are metals with large m^*/m that are not transition elements, it is important to determine whether the glow phenomenon is associated with the larger group (those with large m^*/m), or the subgroup (the transition elements). We can certainly increase the data base by investigating the six metals mentioned above, comparing them to metals with particularly low values of ϵ. Table 4 presents values of ϵ for such a set of materials.

An important consideration in performing such experiments is that the sample must be large enough that an oxygen atom loss can be detected, which was not the case for several of the samples listed in Table 1; for those samples, faint glows were observed but it was unclear whether a significant number of atoms had been removed from the gas stream.

3. Temperature Effects on Surface Glows

The effect of varying surface temperatures on glow intensities was measured for seven different metals. Harteck and co-workers[6-8] observed that it was necessary to cool the metal surfaces that they studied; if the surface temperature increased, the UV intensities became weak. Figures 4 through 6 show that in general there is a peak in the glow intensities, but its position is variable, ranging from 10°C for palladium to 100°C for platinum. Gold occupies a unique position in that the peak is so broad that at the higher temperatures the glow scarcely decreases in intensity, so that at 200°C gold has displaced nickel as the metal with the most intense glow. In fact, platinum behaves similarly, putting the most noble metals in a class by themselves. Another class is obviously occupied by the three contiguous transition elements of the first row of the period chart, Fe, Co, and Ni. Although varying in glow intensity, their temperature profiles are very similar, and quite different from gold and platinum. Palladium behaves in an intermediate way, with the glow intensity decreasing at the higher temperatures, but then turning around in efficiency, whereas aluminum is almost inert.

Since the ordinate in Figures 4 through 6 is referenced to the homogeneous glow at room temperature, the values less than unity for Fe, Co, and Ni at high temperatures mean that the introduction of the surfaces into the flow stream causes a decrease in the homogeneous glow intensity itself. As

18

Table 4

CANDIDATE METALS FOR DETERMINATION
OF UV GLOW GENERATION EFFICIENCY[a]

Metal	$\epsilon \times 10^4$ (cal/mol-deg^2)
Large ϵ	
Mn	14
Sc	10.7
Y	10.2
U	10.0
La	10
V	9.8
Small ϵ	
Sb	0.11
Be	0.17
Bi	0.02
Cd	0.69
Mg	1.3

---

[a]Source: Reference 34
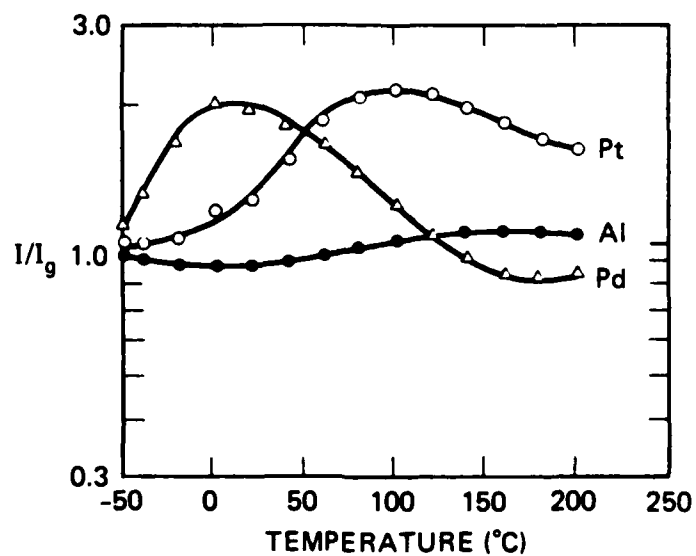
FIGURE 4

RA-330522-1

RELATIVE UV GLOW INTENSITY VERSUS TEMPERATURE FOR Pt, Pd, AND Al

FIGURE 5

RELATIVE UV GLOW INTENSITY VERSUS TEMPERATURE FOR Co AND Au

RA-330522-2

21

FIGURE 6

RELATIVE UV GLOW INTENSITY VERSUS TEMPERATURE FOR Ni AND Fe

22

the introduction of an inert material such as aluminum changes the observed intensities very little, this effect is not geometric; that is, introducing a sample into the field of view of the PM 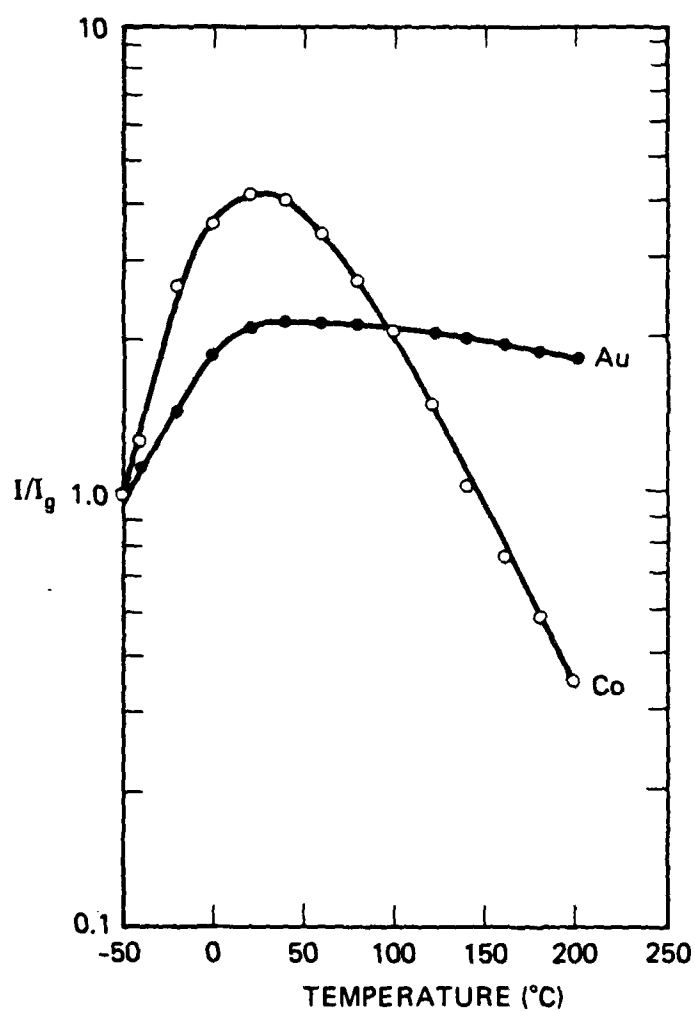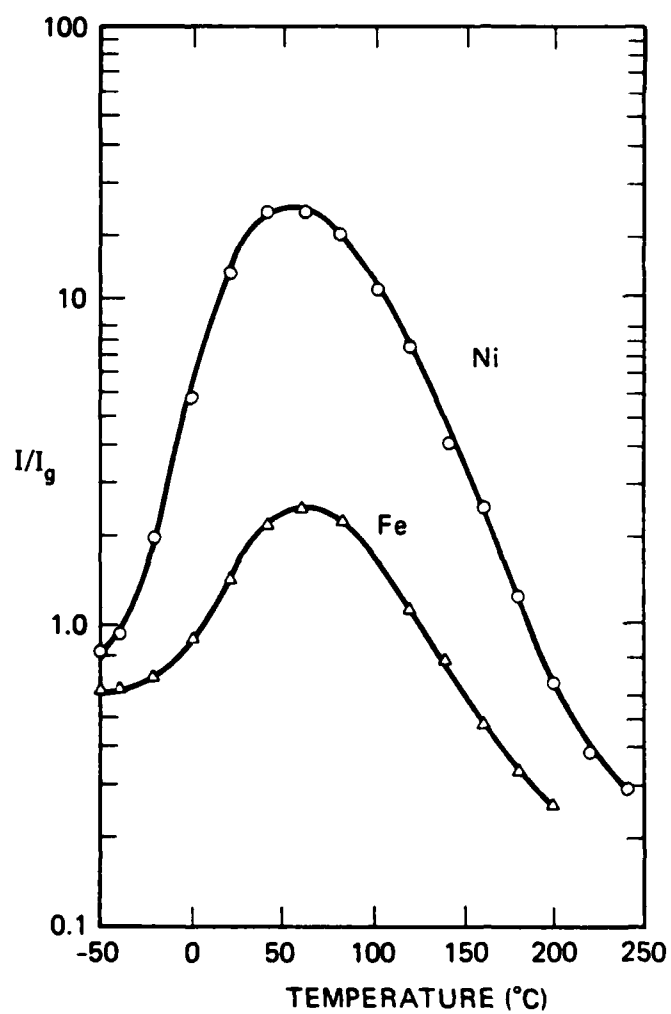tube does not substantially alter the UV flux that it sees. Thus, either the excited molecules are being quenched on the hot surfaces, or the recombination coefficient (γ) for O atoms is increasing, thereby decreasing the atom density available for homogeneous generation of the excited states.

Measurements of the O atom loss at high temperatures for Ni and Co indicate an increasing γ. The alternative hypothesis is in any case unrealistic because the lifetime of an O_2^* molecule is expected to be short, so once it is formed in the gas phase, it is unlikely to be able to reach the surfaces. Given that the homogeneous glow is decreased due to increased γ, one might then expect that the homogeneous glow would be replaced by a more intense heterogeneous one. Because this is not the case with the three metals in question, it must be concluded that the apparent increased rate of heterogeneous atom recombination at the higher temperatures takes place with a greatly decreased efficiency for O_2^* production. This would very likely be reflected in an increasing energy accommodation coefficient. It is shown in the section on $O_2(a^1\Delta_g)$ surface losses that increases are observed for all three transition metals with increasing temperature.

For all the metals except aluminum there is a substantial decrease in glow intensity with decreasing temperature. In this case, no change in heterogeneous O atom loss rate was observed. Although surface mobility of the atoms decreases with temperature, this probably does not provide an explanation, because with a constant flux to the surface, the surface coverage will simply increase, balancing the mobility decrease. A decreasing glow intensity therefore represents a decreasing ratio of O_2^*/O_2 leaving the surface as the temperature decreases. The reason for this is not evident, particularly because there is no apparent increase in $O_2(a^1\Delta_g)$ loss rate with decreasing temperature for any of the metals studied.

4. Auger Spectroscopy

To learn more about the composition of the surfaces, we obtained Auger spectra of various samples. The results are shown in Table 5, where surface concentration ratios are given. Entries labeled (a) are for unetched samples,

Table 5

SURFACE COMPOSITION DETERMINED BY
AUGER SPECTROSCOPY

Sample		Concentration Ratios
316 Stainless	(a)	$O/Fe = 0.93$, $Ni/Fe = 0.11$
	(b)	$O/Fe = 0.97$, $Ni/Fe = 0.14$
Nickel	(a)	$O/Ni = 0.64$
	(b)	$O/Ni = 0.37$
Copper	(a)	$O/Cu = 0.06$, $Cl/Cu = 8.4$
	(b)	$O/Cu = 0$, $Cl/Cu = 5.1$
Gold	(a)	$O/Au = 1.1$
	(b)	$O/Au = 0.02$
Monel	(a)	$O/Ni = 0.56$, $Cu/Ni = 0.67$
	(b)	$O/Ni = 0.13$, $Cu/Ni = 0.25$

Note:

(a) Unetched sample.

(b) Sample subjected to light Ar^+ etch.

whereas entries labeled (b) were subjected to a light argon ion etch, which strips away the first one or two monolayers.

The stainless steel sample shows equal parts of Fe and O, indicating an oxidized layer, which is at least several monolayers thick. The Ni content at the surface is the same as in the bulk material. The nickel sample shows that the oxide layer is principally at the surface, in contrast to steel. The copper surface unexpectedly shows little oxidation, but a great deal of chlorine, even below the surface, so in this case it may be misleading to attribute the Cu data in Table 2 to a metallic surface. The data from the gold sample show an oxide layer in only the top monolayer, as expected for a noble metal. For monel (principally a Ni-Cu alloy), the oxide layer is concentrated in the first monolayer, as with nickel, and there is evidence for enhanced Cu at the surface although thermodynamically the Cu/Ni ratio ought to be 3.5.[35]

We conclude that, in general, the surfaces are oxide layers and that to understand the recombination processes, it is necessary to bear in mind that the typical surface is metallic with chemisorbed oxygen atoms.

5. Spectroscopy of Surface-Generated O_2(A, A', c)

The work of Harteck co-workers[6-8] established that certain metals enhance the recombination of oxygen atoms into electronically excited states. Their UV spectra, while of poor quality, were sufficient to show that the Herzberg I system, O_2(A-X), was the principal emitter.

We have obtained spectra with an image tube-enhanced spectrometer in the visible spectral region, using Ni, Pt, and Co as surfaces, and have obtained considerably more detail. The Ni and Pt spectra, taken with 200 mtorr of O_2, are shown in Figure 7; the Co spectrum has the same appearance. Although the Ni spectrum is 2-3 times more intense, the electronic and vibrational distributions are similar. Thus it is reasonable to conclude that either similar distributions are produced on the two surfaces or the distributions are determined by gas phase collisions after the excited molecule has left the surface, thus washing out the nascent distribution.

Note that the strongest bands in the two spectra are the 0-v" bands of the A-X system, although bands with v'=2 and 3 are noticeable. In fact, when the intensities are divided by the Franck-Condon factors, it becomes apparent
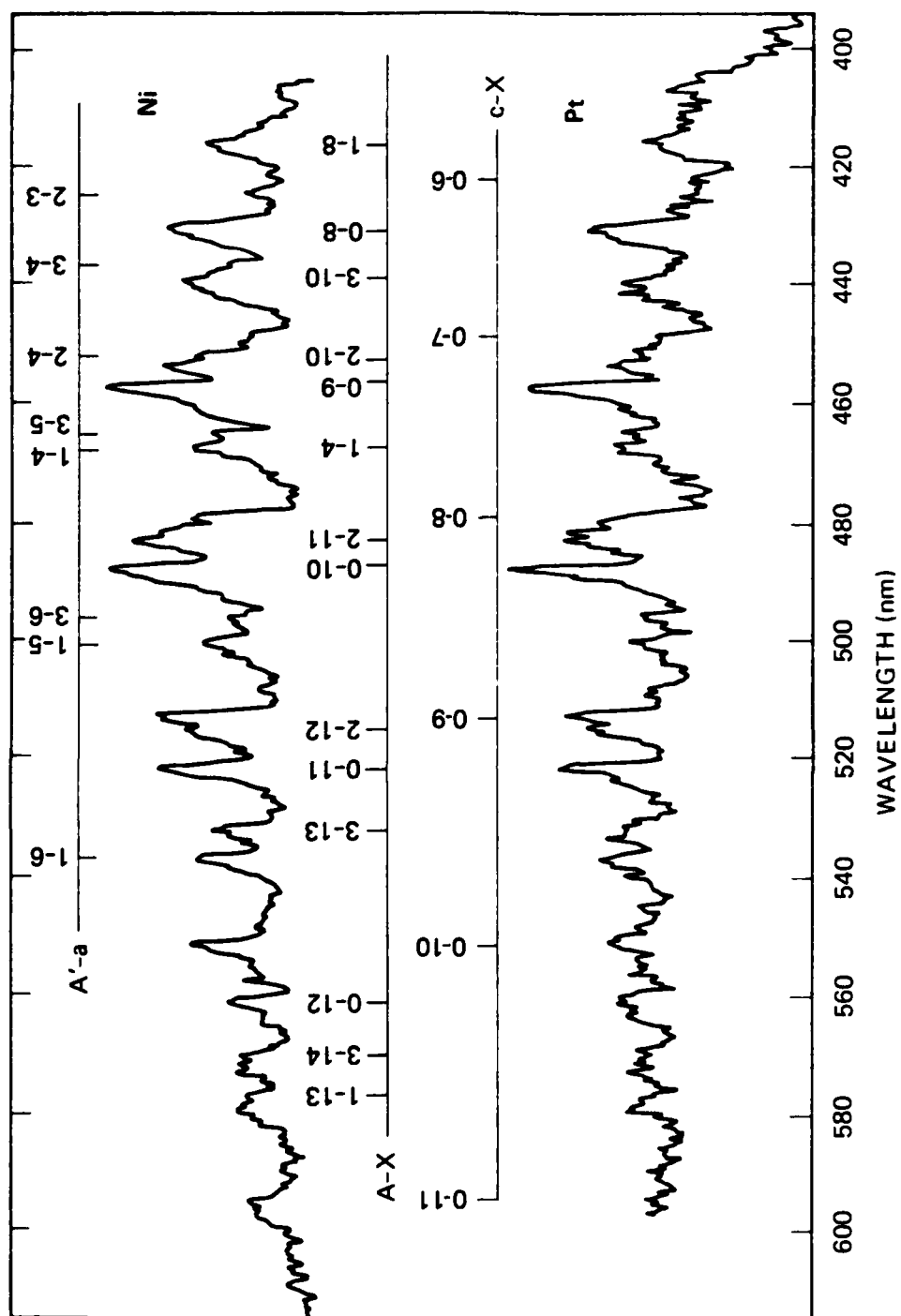
FIGURE 7

SPECTRA OF O_2(A-X, A'-a, AND c-X0 TRANSITIONS OVER Ni AND Pt SURFACES

RA-330522-4

that the higher vibrational levels have higher populations than does v'=0. Bands in the 0-v" progression of the c-X system are strong, with little indication of vibrationally excited levels of $O_2(c)$. On the other hand, <u>only</u> vibrationally excited levels of the A' state are discernible.

Many UV spectra of these systems are available in the literature,[6,27,36-38] obtained under a variety of conditions of pressure and gas composition. It is apparent from analyzing the UV spectra that the state and vibrational distributions, at least in the gas phase, are sensitive to these two parameters. The characteristic of spectra obtained in pure O_2 seems to be that they are vibrationally hotter than those in which Ar or He are present, although there is no existing pure O_2 spectrum in the region above 400 nm for comparison with Figure 7. In our work in this spectral region using an O_2/He afterglow,[31] we found almost no evidence of vibrational excitation, with emission from $O_2(c)$ and $O_2(A')$ in their v'=0 levels being dominant and with relatively weak emission from $O_2(A)$. The absence of $O_2(A')$ v'=0 emission in the present spectra, compared to our earlier results, is particularly striking.

Kenner and Ogryzlo[9] generated emission from the excited O_2 states in the same manner, passing the products from an O_2/Ar discharge through a nickel screen. Comparing their spectrum, reproduced in Figure 8, with that in Figure 7 shows substantial differences. They found considerably more $O(^1S)$ relative to the rest of the emissions, and the $O_2(A-X)$ intensities are even more dominant than in our spectrum. Assuming that nascent vibrational and electronic distributions in the two systems are similar as molecules leave the nickel surface, the difference in the spectra must be due to processes that subsequently take place in the gas phase. The similarity between our nickel and platinum spectra argues that, where the gas phase conditions are the same, the spectra are the same, whereas the difference between our spectra and that of Kenner and Ogryzlo,[9] for the same surface, indicates that it is the gas composition that is the determining factor in the spectral distribution.

Kenner and Ogryzlo have shown,[39] in earlier afterglow studies how critically dependent the spectrum is on gas composition. By increasing the ratio of oxygen atoms to total presssure, they showed that it was possible to pass from a spectrum dominated by c-X emission to one having primarily A-X features. They argued that this effect is the determining factor in explaining why in the terrestrial atmosphere the A-X emission is stronger than c-X,
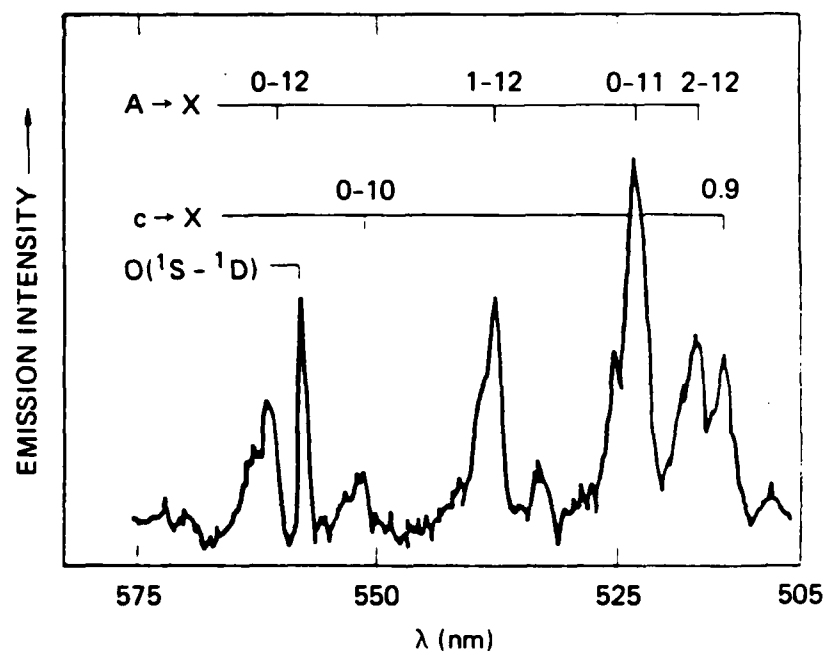
FIGURE 8

RA-330522-5

SPECTRUM OF O_2 GLOW OVER Ni SURFACE (Reference 9)

28

whereas in the Venusian atmosphere, the opposite is the case. It is interesting to note that the spectrum that they display for a high [O]/[M] ratio in a homogeneous system is essentially identical with our surface-generated spectrum.

We thus conclude that: (1) based on the present evidence, the heterogeneous system strongly enhances the O_2 emissions, whereas the spectral distribution is determined by subsequent gas phase interactions, and (2) there is little that can be said concerning the distribution of excited molecules that initially leave the surfaces. This is hardly surprising in view of the fact that these metastable molecules undergo many collisions before they radiate - in order to obtain nascent distributions, it will be necessary to use techniques that do not require waiting for the molecule to emit a photon.

Support for our conclusion comes from recent work by Chu et al,[27] in which the spatial distribution of the O_2 glow originating from a nickel surface was investigated as a function of changing the gas composition. They contend that the $O_2(A)$ that they monitored was not a primary surface-generated product at all, and that in fact there is a precursor, identified by them only as another excited state of O_2. On the basis of our knowledge of the kinetics of vibrationally excited $O_2(A)$, we argue elsewhere that the most likely candidate for this precursor is highly vibrationally excited ground state O_2.

6. Nickel Alloy Studies

Considering the observed variability in excited oxygen state production for the various elemental metals, we decided to investigate the properties of alloys in this respect. Because alloy properties are generally not additive, it was not obvious how they might behave. For this study, we treated various nickel alloys in a similar manner, and the results of the measurements are shown in Figure 9. In spite of uncertainties due to the above-mentioned slow equilibration times, the data clearly show that the O_2^* intensities correlate with the amount of nickel in the sample.

This is interesting not only because it establishes that the property of nickel that results in generation of these states is additive, but also because the data imply that this is not true for other metals. For instance, Monel is 33% copper, a metal that emits no glow and destroys atoms with great efficiency (Table 2). In conjuction with nickel, the copper becomes inert in
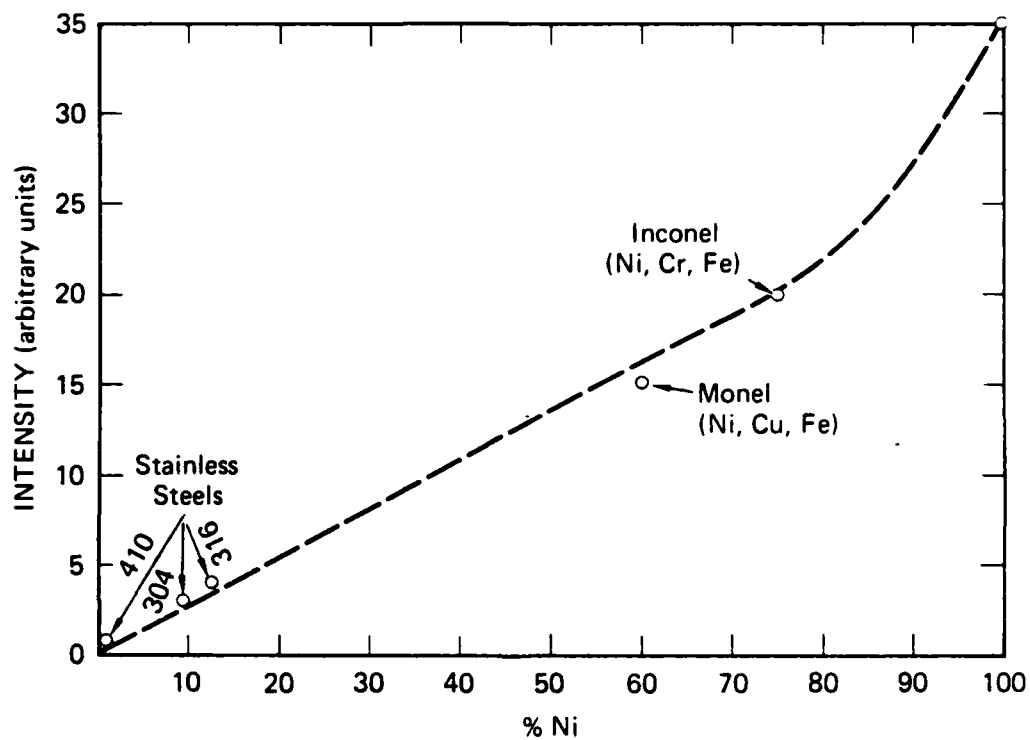
FIGURE 9

UV GLOW INTENSITIES OVER NICKEL ALLOYS

that it neither consumes atoms nor interferes with the effect of the nickel. It would be interesting to extend these measurements to other sets of alloys, particularly to determine whether an alloy can be found with components that are inert to recombination and/or glow production, yet generate the glow as an alloy.

7. Energy Accommodation in Surface Recombination

When atoms recombine on a surface, the resultant molecule initially possesses the recombination energy, 5.1 eV in the case of O_2. The disposition of this energy is one of the most interesting questions in surface physics.

The energy may be disposed of in five possible ways: the molecule may retain the energy in its four degrees of freedom (translational, electronic, vibrational, rotational) or the energy may be transferred to surface phonons, resulting in bulk heating. Considerable data have been amassed to show that in many systems, most of the energy is retained by the molecule. Table 6, reproduced from a paper by Melin and Madix,[40] shows that the energy accommodation coefficient for oxygen atom recombination is generally small. In particular, for nickel (more accurately nickel oxide), 84% of the recombination energy, 4.3 eV, is retained by the O_2. In which of the four possible forms is this energy?

It is probably not in electronic energy, at least not in the 4-5 eV states, because the molecules typically carry away 80-95% of the energy, even where the surfaces appear to be relatively inert to production of the 4-5 eV states. On the other hand, cobalt is one of the more efficient O_2^* producers, yet retains only 33% of the recombination energy. It thus appears that generation of the 4-5 eV states is a relatively minor process in the overall energy disposal.

As for the other two excited states, $a^1\Delta_g$ and $b^1\Sigma_g^+$, the average energy content of the molecules is 4.3 eV, and these two states have electronic energies of 1.0 and 1.6 eV, respectively. Therefore, most of the energy must lie in another form, regardless of the electronic state generated.

Although there is no a priori reason to exclude translational energy as the sink, it would be extremely unusual to find a large fraction of the recombination energy appearing as repulsion of the molecule from the surface.

Table 6

OXYGEN ATOM RECOMBINATION ON VARIOUS METALS[a]

Metal	Recombination Coefficient γ	Energy Accommodation Coefficient
Ag	0.24	0.95
Au	0.008	0.17
Co	0.075	0.67
Cu	0.015	0.30
Fe	0.010	0.07
Ni	0.017	0.16
Pt	0.014	0.10
W	0.013	0.09

[a]Source: Reference 40.

Furthermore, because the process seems to occur with comparable efficiencies with most metals, it is difficult to believe that it would not be well known. Nevertheless, it cannot be excluded for the moment, although an interaction of this type would be easily detectable by time-of-flight measurements.

We are thus left with the rotational and vibrational modes as the most likely forms for the recombination energy, but with the total amount of energy being so large, rotational energy can account for only a small fraction. This can be shown by example: if only $v=1$ and $J=50$ are considered, then the rotational energy content is more than twice as large as the vibrational (for the case of O_2), whereas if $v=10$ and $J=50$, then 80% of the energy is vibrational. Because 4.3 eV corresponds to $v=28$ in the O_2 ground state, it is evident that the vibrational mode is where to look for the energy, which is the case even when considering the a and b states.

If true, this leads to the interesting conclusion that near-surface chemistry under these circumstances should lead to unique products; that is, different products will be obtained when a substrate is acted upon by highly vibrationally excited O_2 than when it reacts with an O/O_2 mixture. The similarly low energy accommodation coefficients for several of the metals shown in Table 5 suggest that they should have comparable catalytic efficiencies for such processes.

The variation in energy accommodation with temperature is usually cast in the form of the Lindemann-Hinshelwood (LH) vs Eley-Rideal (ER) mechanisms, where the former refers to atom migration over the surface until two atoms meet and recombine, and the latter assumes that a gas phase atom pulls off a chemisorbed atom without itself bonding to the surface. Thus, in the ER mechanism, the molecule leaving the surface can have as much energy as the recombination energy minus the metal-oxygen bond energy, that is, a large fraction of the recombination energy. When a small energy accommodation coefficient is measured, it is often proposed that this is a demonstration of the Rideal mechanism, as discussed by Halpern and Rosner[41] for the case of N atom recombination.

With the LH mechanism, the fact that the two atoms must each break a surface bond suggests that less energy is available to the departing molecule. In addition, the concept that both atoms are bonded to the surface as the new

33

bond is forming leads to the idea that energy transfer is likely to be more efficient than in the ER case, also resulting in reduced energy to the new molecule.

Decreasing atomic surface coverage favors the LH over the ER mechanisms. This is because atoms migrating over a surface will eventually find a partner, whereas a gas phase atom striking a bare site will be reflected and fail to recombine. In this way, as temperature increases and surface coverage decreases, it is often proposed that the energy accommodation coefficient will increase, and fewer energetic molecules will leave the surface.

However, a corollary of such a mechanism is that fewer atoms stick to the surface as the temperature is raised and the surface recombination coefficient should decrease. No such effect has been observed; in general more atoms are lost at the higher temperature, paralleling the decreased glow intensity. It therefore appears that although the available recombination energy flux is increasing, less of it can be used to excite the UV glow.

8. Vibrationally Excited O_2 Generated at Surfaces

During other experiments, we searched for evidence of the production of vibrationally excited ground state O_2 ($O_2^\#$) near a nickel surface in the presence of substantial concentrations of atomic oxygen.

In two other systems, we learned that laser-induced fluorescence in the O_2 (B-X) Schumann-Runge transition was an excellent way of detecting $O_2^\#$ over a great range of vibrational levels. We found that in an atmospheric pressure CH_4/O_2 flame, it was possible to detect $O_2^\#$ with great sensitivity over the range v=9-16.[42] It is certainly practical to make these measurements at lower vibrational levels, and from the signal-to-noise ratio in our system and based on the assumption that the distribution is thermal at 2000 K, higher levels can easily be probed up to at least v=20.

In a study of multiphoton dissociation of NO_2 in the 510-532 nm region, we duplicated the experiments of Matsumi et al,[43] showing that very high $O_2^\#$ levels are generated, v=24 being typical. In this instance, we find that these levels are not produced as primary products, but originate in a secondary reaction between NO_2 and a primary species, most probably $O(^1S)$.

34

With this experience, we searched for indications of $O_2^{\#}$ in the region 1 mm above a nickel surface, with oxygen atom densities on the order of 50 mtorr entering the interaction region. With the configuration in use, it was not possible to determine oxygen atom losses caused by the introduction of the metal surface, but a value of 10% for a 1 cm^2 sample is a reasonable estimate. Although this figure may be relatively high in terms of $O_2^{\#}$ generated at a surface (with a flow rate of 1 liter/s, 2×10^{17} molecules/s of O_2 are produced), in a steady-state system, the $O_2^{\#}$ density would be controlled by the dominant loss, which would almost certainly be quenching by oxygen atoms. The rate coefficient for the process

$$O(^3P) + O_2^{\#} \rightarrow O(^3P) + O_2 \tag{3}$$

could be on the order of 10^{-11} cm^3 molec^{-1} s^{-1}, corresponding to a loss rate of 1.6×10^4 s^{-1} at 50 mtorr $O(^3P)$ or a lifetime for $O_2^{\#}$ of 60 μs. It is unlikely that quenching by the majority species, O_2, is nearly as effective as quenching by oxygen atoms because of the lack of energy resonance between high v levels of O_2 and v=0.

The time required for a particle to traverse 1 mm at a total pressure of 1 torr (the pressure of the experiment) can be approximately calculated from the theory of the random walk in three dimensions,[44] which leads to the conclusion that after 60 μs, the most probable position for a particle is 2 mm from its point of origin. Thus, LIF measurements on $O_2^{\#}$ 1 mm from the Ni surface should adequately avoid oxygen atom quenching, unless the rate coefficient is much larger than assumed.

The sensitivity to $O_2^{\#}$ concentrations of the laser-monochromator combination used in these experiments can be approximated from our flame studies. We have not yet conducted an extensive demonstration that the vibrational distribution of O_2 in these flames is thermal; however, because the most intense concentration of $O_2^{\#}$ is found in the burnt gases and not in the combustion region, it seems reasonable that the source of the $O_2^{\#}$ is entrainment of surrounding air. The highest level we have found to date is v=16, a level lying 22,000 cm^{-1} above v=0. On the assumption of 2000 K thermal equilibrium, the ratio [v=16]/[v=0] is 1.3×10^{-7}. As the density of O_2 in air at 2000 K is 7×10^{17} cm^{-3}, the density of O_2(v=16) is then 9×10^{10} cm^{-3} at 1 atm.

Estimating that the burnt gases in the flame contain 10% entrained O_2, the $O_2(v=16)$ density becomes 9×10^9 cm^{-3}. The spectral scan for this level is shown in Figure 10, indicating that it is easily measurable.

Given that 10% of atoms are converted to O_2 at the nickel surface and that there is little quenching of $O_2^{\#}$ within the first 1 mm, the total surface-generated O_2 concentration within that region is estimated to be 2×10^{14} cm^{-3}. From the results of Melin and Madix,[40] the _average_ O_2 molecule carries 4.3 eV energy away with it. If we take the very conservative view that this energy is distributed among six electronic states and the full range of their vibrational levels, then about 1% of the recombined O_2 molecules (2×10^{12} cm^{-3}) is estimated to be in $v=16$ of the ground state. If this were so and if the rotational distribution were no hotter that that for the flame study, an LIF signal far greater than that shown in Figure 10 would result. In fact, no signal was observed for the levels $v=9,16,24$ that we probed.

Because these measurements were obtained during another study, not as much time was devoted to them as would have been necessary to extract small signals from the data. If we accept the Melin and Madix results, and similar results from other laboratories, it is difficult to see where else the recombination energy can reside. One possibility is that generation of vibrationally excited $O_2(a)$ and $O_2(b)$ is more important than $O_2(X)$, and that this energy degrades to $O_2(X)$ in a time long compared with that determined by our viewing geometry. There is at present no LIF technique suitable for detection of these two states. The same can be said for the three Herzberg states, which can only be detected by their feeble radiation; obviously, LIF probing that did not depend on their long radiative lifetimes would offer a great advantage in determining their production rates. Nevertheless, further research on $O_2^{\#}$ detection would be worthwhile. To deal with the problem in its entirety, it is important to measure the various parameters in a single experiment. For example, to be certain of the energy balance, it is necessary to carry out the thermal measurements, determining the oxygen atom loss rate at the surface while also measuring the thermal accommodation coefficient. There is no reason why a concerted effort in this direction could not result in a greatly improved understanding of the system.
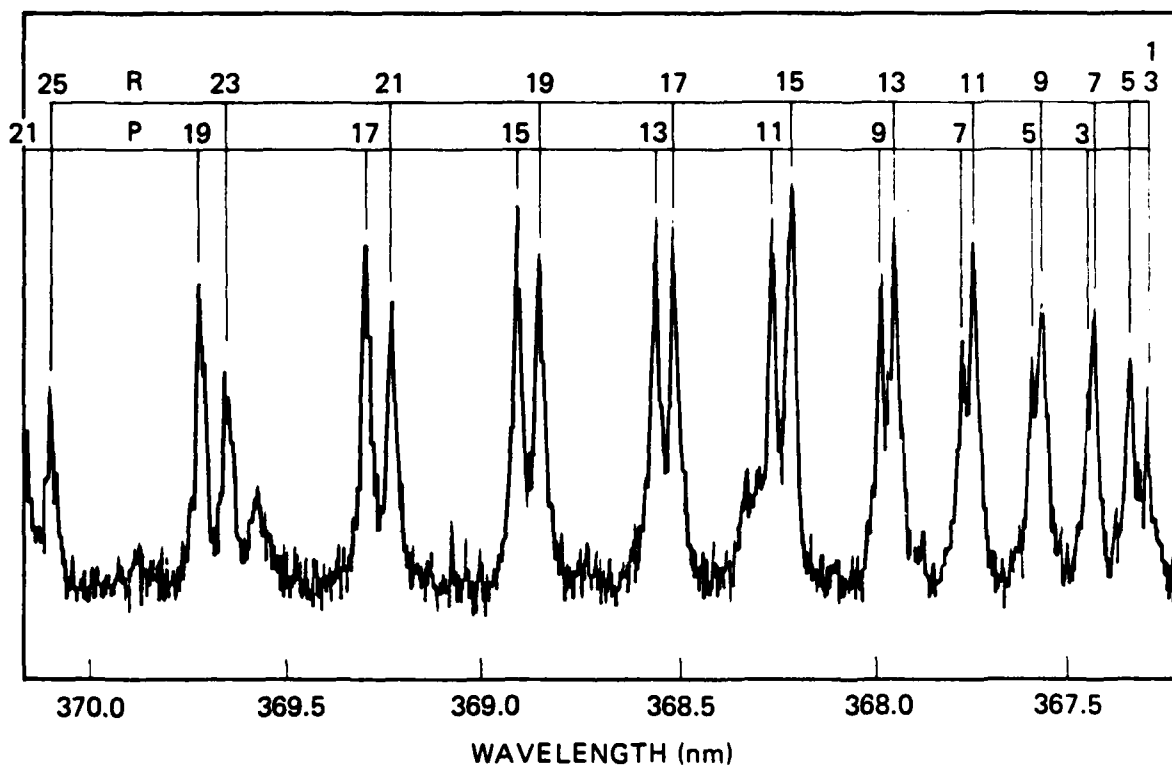
FIGURE 10

LIF SPECTRUM OF $O_2(B-X)$ 0-16 SCHUMANN-RUNGE BAND FROM ATMOSPHERIC PRESSURE CH_4/O_2 FLAME

9. Effects of Enhanced Atom Densities on Surface Glows

The lack of detection of a signal from $O_2^{\#}$ under conditions of greatly enhanced oxygen atom densities above those used for the earlier glow experiments caused us to wonder about the magnitude of the UV glows in such a high atom system. With atom densities in the 1-3 mtorr range, we typically found that the nickel surface would increase the glow intensity by two orders of magnitude over that observed in homogeneous recombination. We expected to see similar enhancements using the intense atom source, in which case it would have been possible to obtain high resolution spectra of these emissions.

In fact, although the homogeneous UV glow was greatly increased with atom densities of ~100 mtorr, approximately linearly with the atom density, the effect of introducing the nickel surface resulted in no glow enhancement. Substantial atom losses were encountered on the nickel surface, typically 30% for a 2-cm^2 sample, and the temperature rose substantially. It is estimated to have been several hundred degrees Celsius, based on observations of wires glowing red.

Thus, we at least have a consistent picture in that high-atom densities led to neither detectable $O_2^{\#}$ densities nor to generation of the high O_2 states. The effect of elevated temperatures was noted in the early work of Harteck et al,[6-8] in which cooling was found to be necessary for UV glow production, and this effect is substantiated by our data in Figure 6.

Nevertheless, this does not necessarily bring us closer to understanding the cause of these observations. The question of the disposition of the recombination energy is still the critical issue, and if the heating of the surface is an indication that some of the energy remains behind, literature results indicate that even at high temperatures, much of the energy is still carried away by the recombined molecules. The work of Melin and Madix[40] was performed at close to room temperature, and thus does not relate to the high atom density data. However, in a more recent study by Halpern and Rosner[41] on N-atom recombination, energy accommodation coefficients were measured at high temperatures on a variety of metals. It was establised that there is considerable variation from surface to surface, but values at the lowest temperatures measured for each metal ranged from 1.0 for Co at 400 K to 0.2 for Re and W at 1400 K. Since the recombination energy of N_2 is 9.8 eV, this means

38

that for the latter case, the departing molecules carry away 8 eV in modes not yet identified.

There is certainly evidence in various systems that recombined molecules carry off internal energy. For example, Kori and Halpern[45] demonstrated that in the recombination of O and CO on a Pt surface, the departing CO_2 carries away more than 2 eV as vibrational energy. We still need to demonstrate such effects for O_2.

10. Contaminant Effects on Energy Accommodation

It is not yet possible to conclude that temperature alone is the cause for lack of detection of either UV glows or $O_2^{\#}$ from the high O atom experiments. The unique feature about the O-atom source is that concentrations of ~100 mtorr in 1 torr O_2 are attained by coating the walls of the discharge region with metaphosphoric acid. Although this may act to prevent wall deactivation to some extent, this cannot be the principal effect, since O-atom wall losses on Pyrex or quartz are not large enough to explain the two order-of-magnitude increase in O atoms that are observed. We presume that there is some chemical interaction in the plasma region that enhances the O atom densities, which at the same time may well lead to system contamination. We have already shown that NO or NO_2 seriously degrade the ability of Ni surface to generate the UV glow, possibly as a result of nitride formation. It would not be surprising to find that in the high O-atom source, generation of metal phosphides might have a similarly deleterious effect on glow production.

We have noted that when a new nickel surface is put into the high-atom system and the discharge is turned on, there is an initial enhancement of the UV glow over the homogeneous glow, by a factor of ~4, and then within a minute the glow is down to the previous level. This can be interpreted as either an effect of increasing temperature, or the result of contaminants from the discharge stopping the activity of the surface. Which cause is in fact responsible will have to be determined by cooling the surface. It would be extremely interesting if it can be demonstrated that in such a system, metal surface temperatures can be controlled by the materials in the discharge stream. From a practical point of view, the possibility of affecting surface temperatures of reentering space vehicles is a very important issue.

39

11. Surface Loss of the $a^1\Delta_g$ State of O_2

We investigated various surfaces to determine their efficiency in deactivating $O_2(a)$. One of the principal goals of the experimental program was to determine the surface reactivity of this molecule with substrate materials although the practical application was related to decontamination problems.

The apparatus used to study production of the higher O_2 states was modified for this series of experiments in two ways. The atoms coming from the discharge were destroyed by a mercuric oxide surface before reaching the test region, so as not to have simultaneous $O_2(a)$ production and loss. The molecule was not detected in the usual manner of monitoring its IR radiation at 1.27 μm, but by measuring its VUV absorption at 128.4 nm, a technique that we had previously developed.

$O_2(a)$ was generated by an O_2 microwave discharge, in which typically 5-10% of the molecules are excited to the $a^1\Delta_g$ state. Because the VUV absorption cross sections have been measured by Ogawa and Ogawa,[4,8] we were able to measure absolute concentrations downstream of the test region, although it was then necessary to estimates the Pyrex wall loss rates to extrapolate back to the concentration at the test surfaces. However, relative loss rates were of more significance than the absolute values. To determine relative destruction rates, we mounted the samples on an aluminum holder and measured the downstream $O_2(a)$ concentrations with and without the samples in the gas stream. It was established that aluminum itself is inert to $O_2(a)$.

The results of room temperature studies are listed in Table 7 in order of decreasing $O_2(a)$ removal efficiency. From comparisons of the loss ratios for a given sample size, it is apparent that the most effective metals are Cu, Ag, and Co, with the next group including Ni, Fe, Pt, and Pd. On a periodic table, these seven metals are contiguous, and what is particularly striking is that this group contains the metals Ni, Pd, and Pt that we have shown to be the most effective at generating the 4-5 eV O_2 states from $O(^3P)$ surface recombination. Harteck and co-workers[6-8] also found Co and Fe to be effective in this respect, so that except for Cu and Ag, there is a qualitative equivalence between those metals generating the 4-5 eV states and those that destroy $O_2(a)$. A realistic model must predict both of these effects, which are in a certain sense contradictory, as effective surface loss of $O_2(a)$ suggests that

Table 7

RELATIVE $O_2(a^1\Delta_g)$ SURFACE LOSS RATES

Surface	$[O_2(a)]_0/[O_2(a)]$	Sample Size
Cu	2.25±0.15	A
Cu(acid-cleaned)	4.77	B
Cu(oxidized)	4.52	B
Ag	2.00	A
Monel(Cu/Ni)	1.90	A
Co	1.90±0.05	A
Fe	1.50±0.05	A
Ni	1.50±0.05	A
Ni(uncleaned)	4.30	B
Ni(acid-cleaned)	4.00	B
Pb	1.34	A
Mn	1.25	A
Sn	1.22±0.02	A
Cr	1.19	A
Mo	1.17±0.03	A
Zn	1.17	A
Ta	1.12±0.03	A
Al	1.10±0.05	A
Hg	1.04	A
Cu	1.53	C
Ni	1.33	C
Pd	1.32±0.03	C
Pt	1.27	C
Rh	1.19±0.02	C
Ir	1.10±0.08	C
Sc	1.10±0.04	C
In	1.07±0.05	C
Au	1.06±0.03	C
W	1.05±0.02	C
Ti	1.05±0.03	C
Zr	1.05	C
Scotchguard	1.04	A
PVC	1.05	A
Graphite	1.28	1.4"x2"
Alumina	1.04	A

Sample Sizes   A   2"x2"
                   B   cylindrical configuration
                   C   1"x1"

41

there is good coupling between the O_2 and surface phonons, whereas surface generation of O_2^* without energy accommodation indicates the opposite.

The data in Table 7 also show that the $O_2(a)$ destruction efficiency is independent of gross surface treatment, which implies that in all cases the surfaces affected by the $O_2(a)$ are metallic oxides, not an unexpected conclusion. Of the substantial number of organic materials tested, all have activities comparable to those of the most inert metals.

12. Temperature Effects on Surface Destruction of $O_2(a^1\Delta_g)$

Figures 11 through 13 show data on the response of the downstream $O_2(a)$ concentration to introduction of temperature-controlled metal surfaces. There are some differences in sample size, which should be noted when making comparisons, and the expected logarithmic relationship was not observed between $O_2(a)$ loss and surface area, presumably a consequence of the flow patterns in the reaction cell. To compare equal size samples, reference should be made to Table 7. Because a calculated surface loss rate coefficient (γ) would from our data appear to depend on surface area, these values have not been tabulated. However, it is useful to estimate the size of γ, because it is generally much larger than values quoted for Pyrex surfaces.[49] This can be obtained by comparison with oxygen atom loss on surfaces for which γ is known. Greaves and Linnett[50] quote a value for γ of 0.028 for O-atoms on Ni, for which we typically find O-atom losses of 30% for an 8-in^2 sample. Figure 13 shows such a loss ($I_0/I = 1.4$) at about room temperature on the same size sample, so the γ in the two cases is comparable (slightly larger for $O_2(a)$, as its velocity is less). However, it is more instructive to compare the profiles in Figures 11 through 13.

Some hysteresis effects were observed, although they did not seriously affect the data. For consistency, each experiment was performed by bringing the samples up to the high temperature, then taking data as the temperature was reduced down to the lowest point.

Various effects were observed for the surfaces investigated. Silver has by far the highest loss rate at low temperatures, but is much less effective in removing $O_2(a)$ at high temperatures. At 200°C, it is exceeded in efficiency by almost every other metal except Al. Nickel is inert compared with
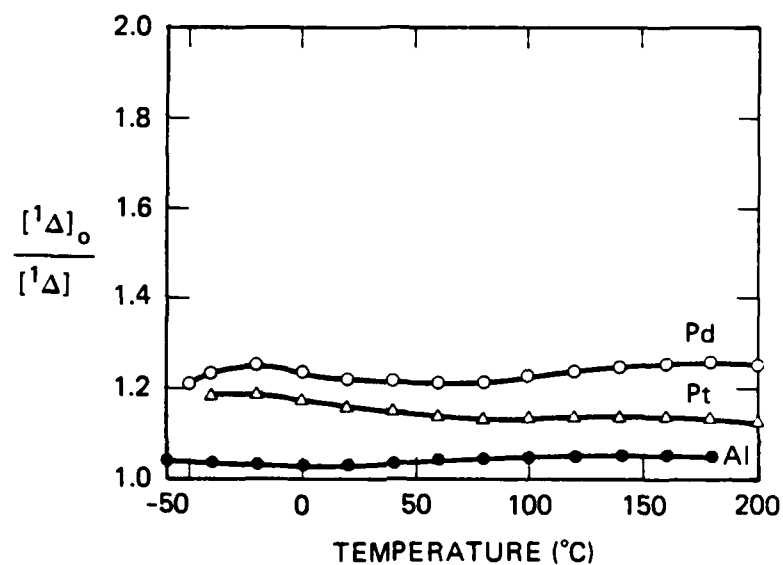
FIGURE 11

$O_2(a^1\Delta_g)$ LOSS VERUS TEMPERATURE ON Pt ($1\text{-}in.^2$), Pd($1\text{-}in.^2$), and Al ($8\text{-}in.^2$). THE ORDINATE IS THE RATIO OF DOWNSTREAM $[O_2(a)]$ BEFORE SAMPLE INTRODUCTION TO THAT WITH SAMPLE IN PLACE

43
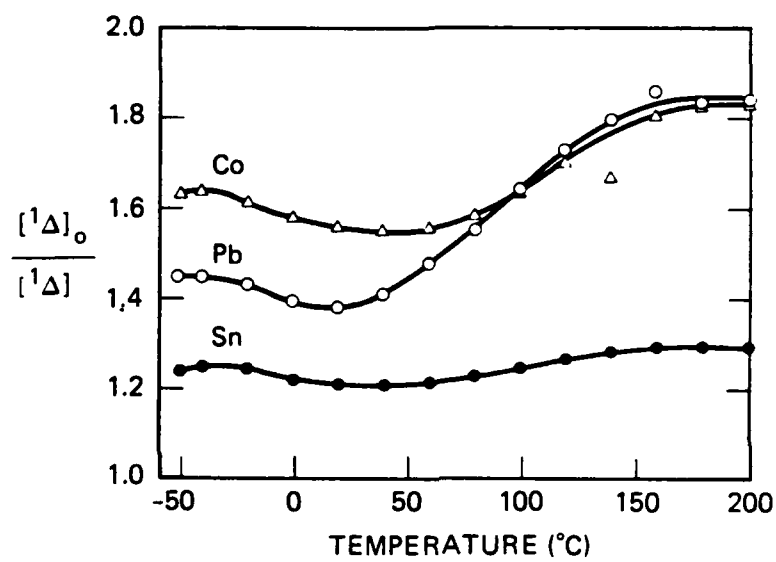
RA-330522-9

FIGURE 12

$O_2(a)$ LOSS VERSUS TEMPERATURE ON Co, Pb, AND Sn (all 4-in.^{2})

44
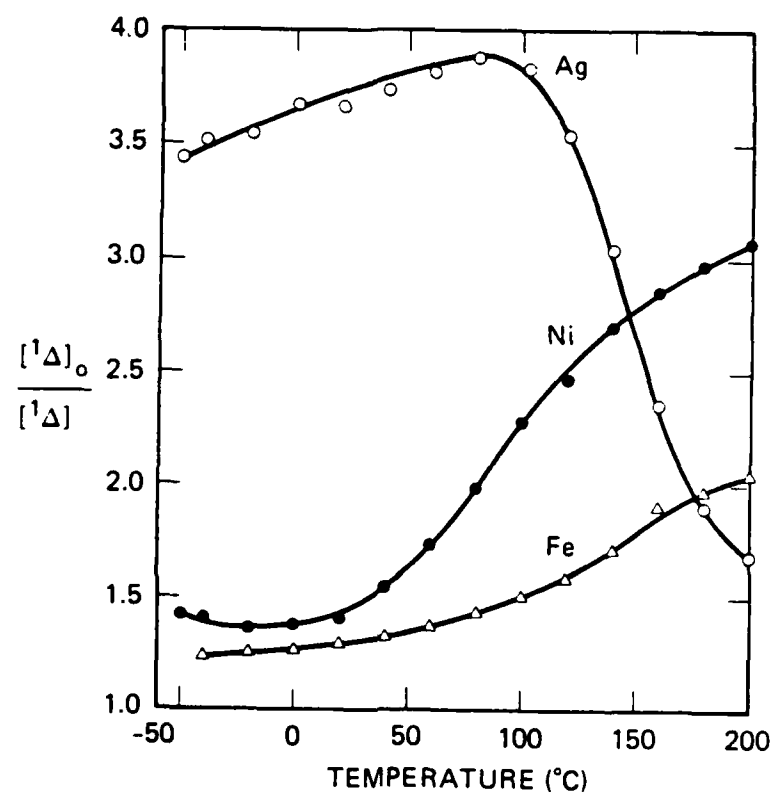
FIGURE 13

RA-330522-10

$O_2(a)$ LOSS VERSUS TEMPERATURE ON Ag, Ni, AND Fe (all 8-in.^{2})

45

silver at low temperatures, but becomes the most active metal at high temperatures. Lead, which had little activity in UV glow generation, has considerable activity in $O_2(a)$ destruction at 200°C. Aluminum, as always, is inert.

With such effects, it is evident that the comments in the previous section pointing out the similarity, at 300 K, between those metals that exhibit effective UV glow generation and those that show high $O_2(a)$ destruction efficiency, are not illuminating. Because ordering the various metals in terms of $O_2(a)$ destruction effectiveness depends on temperature, there is not enough information to draw valid conclusions.

It is interesting to note that most of the materials do not exhibit monotonic behavior with temperature. Thus, the maximum in $O_2(a)$ destruction efficiency observed for silver at 80°C seems to occur for nickel at higher temperatures (250°C), whereas Pb and Co appear to reach a maximum at 200°C.

In comparing different metals, one obvious area where our knowledge is minimal is in understanding how the $O_2(a)$ is quenched at the surfaces. Reaction is one possibility; presumably the excited molecule is a more efficient oxidizer than ground state O_2. It is possible that interaction with chemisorbed O_2 on the surface converts the 1 eV electronic energy to the equivalent vibrational energy in the ground state (v=5), a process invoked by Parker[51] for homogeneous $O_2(a)$ quenching. Another scenario is that the energy is coupled to the lattice on collision, resulting in a high value for the energy accommodation coefficient, and in principle the electronic energy could also be converted to recoil energy, resulting in fast O_2 molecules leaving the surface. From only the data shown in Figures 11 through 13, it is not possible to sort out these alternatives. Probing the vibrational temperature of the molecules near the surface would be most helpful in clarifying these issues because vibrational energy can be considered as one of the last repositories of the energy content of a system. Ultimately, transfer to kinetic energy occurs, but usually this is a slow process, so detection of vibrational energy in the ground state of a molecule should provide one of the best clues to internal energy content (for molecules such as O_2 and N_2, where radiative channels are rarely important).

III   DISCUSSION

This discussion is limited to the unpublished material, involving oxygen atom recombination and $O_2(a^1\Delta_g)$ loss on metal surfaces. The major results of this study are summarized below

(1) Practical surfaces can be characterized in terms of the production and loss processes that were studied. In other words, even though the measurements were performed at substantial pressures and the surfaces were oxidized to some degree, each surface has a fairly unique signature. This is particularly true for the temperature studies and is a strong indication that the measurements are related to some aspect of the substrate properties. Thus, it cannot be argued that at the pressures used, physically absorbed O_2 molecules and system contaminants mask the true interactions between the surfaces and the atoms and excited molecules. It has not yet been demonstrated that this is the case for the high intensity oxygen atom source, where contamination may play an important role.

(2) There are apparent correlations between the effectiveness of metals in generating the UV glow and certain physical properties of the metals. In particular, we have shown that the electronic heat capacity of metals bears some relationship to the UV glow, at least at 300 K. An extended survey, using a group of metals selected for their high and low electronic heat capacities, would substantiate whether this correlation is predictive and therefore useful.

(3) The high temperature ($T < 250°C$) behavior of the various metals in terms of UV glow generation seems to be related to their periodic chart grouping. The three transition elements Fe, Co, and Ni, although having considerably different efficiencies for generating the glow, exhibit the same temperature profile, with a sharp

extinction of glows taking place in the 100-200°C region. On the other hand, the noble metals Pt and Au show only a slight decrease in glow production on heating, becoming more effective than the best room temperature surface, Ni, above 160°C.

(4) Comparisons of UV glows from nickel alloy surfaces, indicate that their intensity is proportional to the fraction of nickel in the alloy, regardless of the other components. This again demonstrates the sensitivity of glow production to the substrate, as opposed to adsorbed materials.

(5) In the destruction of $O_2(a^1\Delta_g)$ on metal surfaces, 300 K data suggest similarities to the UV glow process in that the same metals are effective in the two systems. Furthermore, at high temperatures the transition elements Fe, Co, and Ni become even more effective. Very interesting behavior is shown by silver, which is highly effective at destroying $O_2(a)$ below 100°C, but becomes ineffective by the time the temperature has reached 200°C. On the other hand, the usually inert lead shows considerable activity, particularly at high temperature. It is clearly important, both in the $O_2(a)$ and UV glow studies, to instrument the system so that it is possible not only to observe the generation and loss of the excited O_2 species, but also to determine how energy accommodation varies with temperature and to search for the species expected to be the prime carrier of energy away from these surfaces, vibrationally excited O_2. We have demonstrated our ability to measure $O_2^{\#}$ over a wide range of vibrational levels.

(6) Application of Auger spectroscopy has shown that chemisorbed oxygen is in general limited to the top monolayer of these surfaces, the ratio of oxygen to metal atoms being sharply lower in the next layer. Thus, the metal is exposed even in the top layer to incoming atoms and $O_2(a)$, and we are reasonably justified in claiming that this work refers to recombination on metal, rather than oxide, surfaces.

48

(7)   Spectra of 400-600 nm emission were obtained from O atom
      recombination on Ni and Pt surfaces. There is no substantial
      difference between the electronic state and vibrational energy
      distributions in these two cases. By comparison with published
      surface-generated spectra, it is clear that the distributions are
      determined by the gas phase composition, not by the heterogeneous
      recombination process itself. Thus, it cannot as yet be proven
      that the molecule that ultimately radiates is in fact produced at
      the surface. Precursor molecules have been proposed, and it seems
      most likely that, if there is a precursor, it must be a highly
      vibrationally excited molecule, possibly in the ground electronic
      state. Published data indicate that 300 K energy accommodation
      coefficients for many of the metals that we investigated are very
      low, typically 10%. There is thus every reason to expect that
      large fluxes of highly excited molecules are leaving the surfaces;
      their identity is yet to be determined.

(8)   Although most experiments were conducted in the 1-5 mtorr $O(^3P)$
      range, we have now developed a source that is capable of producing
      100-150 mtorr $O(^3P)$ at 1 torr total pressure. Preliminary
      indications show that, although the homogeneous UV glow is strongly
      enhanced at these high atom densities, there is no UV glow
      associated with recombination on a nickel surface. As we have
      shown how sensitive this process is to temperature, it is not
      surprising to find that the very hot surface that develops under
      these conditions is not conducive to generation of the UV glow.
      However, the possibility also exists that contamination associated
      with reactions in the microwave discharge has a deleterious effect
      on glow generation. It is of great interest to determine whether
      in such an experiment the recombination energy is retained by the
      metal or whether it leaves the surface with the molecule. It is
      yet to be determined whether cooling the surface will result in a
      greatly enhanced UV glow, which would then distinguish between
      thermal and contaminant effects.

IV RECOMMENDATIONS

The critical issue in the interaction of surfaces with excited molecules, either formed _in situ_ as in atom recombination or transported to the surface, is the disposition of the energy. We have only scratched the surface, so to speak, in studying these effects with oxygen because we believe that the energy associated with the molecules radiating in the UV is only a fraction of the recombination energy, whereas other experiments indicate that most of this energy is carried away by the recombined molecule. The first priority is to learn whether, as we suspect, the active energy mode is the vibrational one. Such experiments will involve incorporation of a dye laser into the system.

Considerable credence has been given to the energy accommodation coefficient measurements presented by Melin and Madix,[40] which have shown that at 300 K, oxygen atoms result in low values on a number of surfaces. To our knowledge, no further work has substantiated these results, and before extensive measurements are made, it makes sense to demonstrate that indeed most of the recombination energy is not tranferred to the surfaces.

It is important to identify the physical and/or chemical properties of the metals that determine their reactivity. Measuring production or loss of excited species at a single temperature can be misleading. It appears that temperature profile shapes for UV glow production may characterize groups of elements, and these measurements should be extended beyond those that we have investigated. The apparent correlation between those metals producing UV glows and their electronic heat capacity should be studied further. As a consequence of what we have observed so far, predictions have been made of which uninvestigated metals might be particularly effective in generating the UV glow and which can be expected to be relatively inert.

The study of the temperature dependence of the $O_2(a)$ surface losses should be extended. The measurements obtained in this study are the most quantitative to date on the temperature effects for both O_2^* production and $O_2(a)$ loss, and it would be instructive to investigate $O_2(a)$ loss at higher

temperature (under these conditions the UV glows are extinguished). At the same time, it is desirable to follow by thermal measurements the energy accommodation coefficient, as well as the surface-generated flux of $O_2^{\#}$.

REFERENCES

1. S. B. Mende, O. K. Garriott, and P. M. Banks, Geophys. Res. Lett. 10, 122 (1983).

2. S. B. Mende, P. M. Banks, and D. A. Klingelsmith, Geophys. Res. Lett. 11, 527 (1984).

3. S. B. Mende and G. R. Swenson, "Vehicle Glow Measurements on the Space Shuttle," NASA Confernce Publication 2391 (May 1985).

4. J. H. Yee and V. J. Abreu, Geophys. Res. Lett. 10, 126 (1983).

5. T. G. Slanger, Geophys. Res. Lett. 10, 130 (1983).

6. R. R. Reeves, G. G. Mannella, and P. Harteck, J. Chem. Phys. 32, 946 (1960).

7. G. G. Mannella, R. R. Reeves, and P. Harteck, J. Chem. Phys. 33, 636 (1961).

8. G. G. Mannella and P. Harteck, J. Chem. Phys. 34, 2177 (1964).

9. R. D. Kenner and E. A. Ogryzlo, Int. J. Chem. Kin. 12, 501 (1980).

10. R. D. Kenner and E. A. Ogryzlo, Can. J. Phys. 61, 921 (1983).

11. R. D. Kenner and E. A. Ogryzlo, Can. J. Phys. 62, 1599 (1984).

12. W. J. Fastie, comments at Physics of Spacecraft Glow Workshop, Huntsville, AL (Jan. 1984).

13. M. R. Torr, P. B. Hays, B. C. Kennedy, and J. C. G. Walker, Planet. Space Sci. 25, 173 (1977).

14. F. C. Witteborn, "Ground-based IR Photometry of STS-9", Physics of Spacecraft Glow Workshop, Huntsville, AL (Jan. 1984).

15. V. J. Abreu, W. R. Skinner, P. B. Hays, and J.-H. Yee, "Optical Effects of Spacecraft-Environment Interaction: Spectrometric Observations by the DE-B Satellite", AIAA Shuttle Environment and Operations Meeting, Washington D. C. Nov. 1983.

16. G. R. Swenson, S. B. Mende, and K. S. Clifton, Geophys. Res. Lett. 12, 97 (1985).

17. M. Mizushima and T. Shimazaki, Planet. Space Sci. 33, 1119 (1985).

18. B. D. Green, Geophys. Res. Lett. 11, 576 (1984).

19. F. Bylicki, J. G. Weber, H. Zscheeg, and M. Arnold, J. Chem. Phys. 80, 1791 (1984).

20. V. M. Donnelly and F. Kaufman, J. Chem. Phys. 66, 4100 (1977).

21. O. Cheshnovsky and A. Amirav, Chem. Phys. Lett. 109, 368 (1984).

22. S. E. Schwartz and H. S. Johnston, J. Chem. Phys. 51, 1286 (1969).

23. P. B. Sackett and J. T. Yardley, J. Chem. Phys. 57, 152 (1972).

24. K. Papadopoulos, Radio Sci. 19, 571 (1984).

25. T. G. Slanger, Geophys. Res. Lett. 13, 431 (1986).

26. I. C. McDade, E. J. Llewellyn, R. G. H. Greer, and G. Witt, Can. J. Phys. 62, 780 (1984).

27. A.-L. Chu, R. R. Reeves, and J. A. Halstead, J. Phys. Chem. 90, 466 (1986).

28. E. A. Ogryzlo, J. Photochem. 25, 389 (1984).

29. M. R. Torr, D. G. Torr, and R. R. Laher, J. Geophys. Res. 90, 8525 (1985).

30. G. Black and T. G. Slanger, J. Chem. Phys. 74, 6517 (1981).

31. T. G. Slanger, J. Chem. Phys. 69, 4779 (1978).

32. T. G. Slanger and D. L. Huestis, J. Geophys. Res. 86, 3551 (1981).

33. T. G. Slanger and D. L. Huestis, J. Geophys. Res. 78, 2274 (1983).

34. C. Kittell, Introduction to Solid State Physics, p. 259, John Wiley and Sons, N.Y. 2nd. ed. (1962).

35. P. Van der Plank and W.M.H. Sachtler, J. Catalysis, 12, 35 (1968).

36. R. J. McNeal and S. C. Durana, J. Chem. Phys. 51, 2955 (1969).

37. V. Degen, S. H. Innanen, G. R. Hebert, and R. W. Nicholls, Identification Atlas of Molecular Spectra, 6. The O_2(A-X) System, York University, 1968.

38. C. A. Barth and M. Patapoff, Astrophys. J. 136, 1144 (1962).

39. R. D. Kenner and E. A. Ogryzlo, J. Photochem. 10, 199 (1979).

40. G. Melin and R. J. Madix, Trans. Faraday. Soc. 67, 198 (1971).

41. B. L. Halpern and D. E. Rosner, JCS Faraday Trans. I 74, 1883 (1978).

42. R. A. Copeland, D. R. Crosley, J. B. Jeffries, and T. G. Slanger, "Laser-Induced Fluorescence Spectra in Flames of High Vibrational Levels of Ground State O_2", in preparation.

43. Y. Matsumi, Y. Murasawa, K. Obi, and I. Tanaka, Laser Chem. 1, 113 (1983).

44. S. W. Benson, The Foundations of Chemical Kinetics, p. 546, McGraw-Hill Book Co. New York, 1960.

45. M. Kori and B. L. Halpern, Chem. Phys. Lett. 110, 223 (1984).

46. D. E. Rosner and H. H. Feng, JCS Faraday I, 70, 884 (1974).

47. T. G. Slanger and G. Black, Geophys. Res. Lett. 8, 535 (1981).

48. S. Ogawa and M. Ogawa, Can. J. Phys. 53, 1845 (1975).

49. L. Elias, E. A. Ogryzlo, and H. I. Schiff, Can. J. Chem. 37, 1680 (1959).

50. J. G. Parker, J. Chem. Phys. 67, 5352 (1977).

APPENDIX A

CONJECTURES ON THE ORIGIN OF THE SURFACE GLOW OF SPACE VEHICLES

Tom G. Slanger

Molecular Physics Laboratory, SRI International, Menlo Park, CA 94025

CONJECTURES ON THE ORIGIN OF THE SURFACE GLOW OF SPACE VEHICLES

Tom G. Slanger

Molecular Physics Laboratory, SRI International, Menlo Park, CA 94025

Abstract. It is argued that a plausible identification of the surface-originating glow that has been observed on the AE-E satellite and the space shuttle between 140 and 400 km is the OH Meinel band system. The emission appears to be generated by surface interaction with 5 eV $O(^3P)$ atoms at high altitude, and with 10 eV O_2 molecules below 160 km. The primary factors that favor this identification are the apparent spectral distribution and the deduced radiative lifetime, and if valid, implies that the total equivalent surface brightness of the vehicles is on the order of 10 MR, mainly in the near infrared.

In recent articles by Yee and Abreu (1982, 1983), observations made from the Atmospheric Explorer (AE-E) satellite are described which indicate that there is a source of optical emission that originates on the satellite itself. It is the purpose of this letter to discuss the effect and to suggest a possible explanation. The recent spectacular photographs of a similar phenomenon on the space shuttle (Banks, et al, 1983; Aviation Week and Technology, 1982) indicate that the mechanisms are probably the same.

The data of Yee and Abreu, confirmed by the space shuttle photographs, show that the emission is a strong function of the angle between the spacecraft velocity vector and either the direction of view or the surface being viewed. The most intense radiation comes from surfaces facing the direction of motion, from which one can immediately hypothesize that the emission is caused by collisions with the particles of the ambient atmosphere, which strike the surfaces at 8 km s^{-1}.

The data presented by Yee and Abreu cover the altitude range of 140-280 km, and the satellite measured N_2 and $O(^3P)$ densities at the same time as the photometric studies were made. As pointed out by these authors, it is quite evident from the two sets of data shown that in the 160-280 km range there is a strong correlation between emission intensity and oxygen atom density; their scale heights are 35 ± 2 km. Thus, it seems most likely that surface interactions with oxygen atoms instigate the emission process.

At altitudes below 160 km another effect seems to set in; the intensity becomes uncoupled from the local atom density, and rises much faster than the density. The questions to be answered are, what is the particle emitting the radiation, and how is it produced?

The two strongest pieces of evidence that suggest the identity of the emitter are the wavelength of the radiation, and the dimensions of the radiating region. The data of Yee and Abreu

were taken at 6563 Å and 7320 Å, with more intensity at the longer wavelength. The space shuttle glow appears orange in the photograph and it is reported that the radiation all seems to be above 6000 Å (Banks, 1982).

The size of the radiating region is a measure of the radiative lifetime of the emitter. A particle with an available allowed transition will exhibit a radiative lifetime of $10^{-5} - 10^{-8}$ sec, a range of times so short that an excited particle generated at the surface will radiate there, and would therefore not be detected by the photometer on the AE satellite. On the other hand, metastable particles will exhibit lifetimes 10^{-3} sec or longer, and such particles leaving the surface will cause a halo to appear around the spacecraft.

The space shuttle photograph shows that the glow is not localized at the surfaces; it extends out to at least 20 cm from the skin. At the tip of the tail, there is a fan-shaped glow, which appears to extend for meters. Thus, the emitter has a relatively long lifetime, an exact value for which can be extracted from the observations only by making an assumption about the velocity of the particle leaving the surface. Yee and Abreu made such a calculation, based on the fall-off of intensity as the photometer scanned away from the spacecraft velocity vector. They concluded that the data were best fit by assuming a particle velocity of 2×10^5 cm s^{-1} and a radiative lifetime of 5×10^{-3} s. The product of these two figures is 10 meters, so the glowing region is quite extensive, and larger than indicated by the space shuttle photographs, although the dynamic range of the film should be considered in interpreting the thickness of the halo in the latter case.

A lifetime of 5 ms provides a distinct limitation on the particle identity. For instance, it is inconsistent with any known transition in O_2, the species initially suggested as the most likely candidate for the emitter. The forbidden transitions in O_2 vary in lifetime from 0.15 s for $O_2(A^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-)$ to 3800 s for $O_2(a^1\Delta_g \rightarrow X^3\Sigma_g^-)$, so a value of 5 ms is outside this range. Furthermore, visible emission from metastable O_2 produced by surface recombination will be blue (Harteck and Reeves, 1964), not the red or orange indicated by the space shuttle and AE satellite data. The orange glow in the space shuttle photographs appears to be the true color, since limb scans taken at the same time showed a green airglow, the characteristic OI (5577) green line.

On the assumption that the emitter is not O_2, but is a species chemically formed by oxygen atom bombardment, at least in the altitude region where the intensity is a linear function of the $O(^3P)$ density, then the most likely small molecule is OH. Although positive identification must ultimately come from spectroscopic observation, the evidence that can be marshalled in sup-

port of this identification is quite compelling.

In the first place, it would not be surprising to find OH produced. The relative energy of the oxygen atoms hitting the surface is 5 eV, and although no relevant data exist, it is not unreasonable to expect interaction between these atoms and adsorbed water and/or C-H bonds in the construction materials, i.e.

$$O(^3P)^* + H_2O(ads.) \rightarrow OH + OH \qquad (1)$$

$$O(^3P)^* + R-H \rightarrow R^{\cdot} + OH \qquad (2)$$
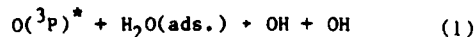
In the gas phase, process (1) is 0.8 eV endothermic, and process (2) is roughly thermoneutral, so there is a great deal of excess energy available. OH is unique among diatomic molecules in the fact that high overtones of its vibration-rotation spectrum are relatively intense. These bands (the Meinel system) are observed in the red spectral region, and are extremely strong in the terrestrial nightglow (Broadfoot and Kendall, 1968), being generated by the reaction between H and O_3. The emission from that reaction commences at ~6000 Å, and corresponds to a high level of vibrational excitation ($v \leqslant 9$) [Streit and Johnson, 1976].

If we hypothesize that the atom-surface interaction gives a similar OH vibrational distribution, then the "spectrum" is consistent with observations. The two wavelengths investigated by Yee and Abreu, 6563 Å and 7320 Å, correspond to the 6-1 and 8-3 OH bands, respectively. The $v = 6$ level has a 6 ms radiative lifetime, the $v = 8$ level has a 4 ms lifetime [Mies, 1974], values that neatly bracket the lifetime deduced by Yee and Abreu. If the OH vibrational distribution were similar to that from the H + O_3 reaction, then twice as much intensity would be expected at 7320 Å than at 6563 Å (Streit and Johnson, 1976), approximately as observed.

The excellent correlation between $[O(^3P)]$ and light intensity down to 160 km suggests that only $O(^3P)$ is responsible for the radiation. There are, however, other species present, the atmosphere at that altitude being basically a three-component system - $O(^3P)$, N_2, O_2. At 250 km, 80% of the particles are $O(^3P)$, 19% are N_2, and 1% are O_2. At 165 km, 50% are $O(^3P)$, 45% are N_2 and 5% are O_2. Since over the range where N_2 has increased from 19% to 45% the intensity is proportional only to $O(^3P)$, it must be concluded, as did Yee and Abreu, that bombardment of the surface by 9 eV N_2 molecules does not contribute to the radiation, i.e. that the effect is not an indiscriminate energy absorption phenomenon.

However, below 165 km, where the radiation scale height decreases, it becomes very similar to the N_2 scale height. As N_2 is apparently not involved, the obvious candidate is O_2, which is hitting the surface with 10 eV relative energy, and has a scale height even smaller than that of N_2. Since there is much less O_2 than $O(^3P)$, the implication is that OH is generated much more efficiently by 10 eV O_2 than by 5 eV $O(^3P)$. Thus, as an empirical function, it would be reasonable to try the relationship

$$\text{Intensity} = K \ [O(^3P)] + A[O_2] \qquad (3)$$

where K is a proportionality constant and A is the factor by which 10 eV O_2 generates OH more

effectively than 5 eV $O(^3P)$. The data presented by Yee and Abreu only show the measured $O(^3P)$ and N_2 profiles. To fit equation (3) an O_2 profile is needed. One given by Ackerman et al. (1974) was selected, since in that work an N_2 profile is also given which exhibits an identical scale height to that of Yee and Abreu. The O_2 data, obtained by UV absorption measurements, extend to 190 km, and parallel the 800 K O_2 model of Jacchia (1971).

The data of Yee and Abreu are presented in two ways. The primary data of intensity vs altitude are given for the two wavelengths, then the averaged data for individual altitudes is presented, at approximately every two kilometers. The best curves drawn through the primary data do not give a line exhibiting the abrupt change in slope that they have drawn through their averaged data, so we have chosen to fit the former.

Fig. 1 shows the line calculated from equation (3), using $K = 1.2 \times 10^{-8}$ rayleighs cm^3 and $A = 4$, and the primary data points of Yee and Abreu [1982] (their Fig. 2a). The agreement is satisfactory, the deviation being largest at high altitude where the error bars on the intensity measurements are largest. The sensitivity of the line to the choice of A is such that if K is adjusted so as to keep the high altitude intensity constant, then varying A from 2 to 4 to 8 causes the intensity at 140 km to increase from 320 to 410 to 580 rayleighs. Thus, the form of the profile can be reproduced by hypothesizing that the emitter is generated by surface collisions with both 5 eV $O(^3P)$ and 10 eV O_2, the latter being approximately four times as effec-

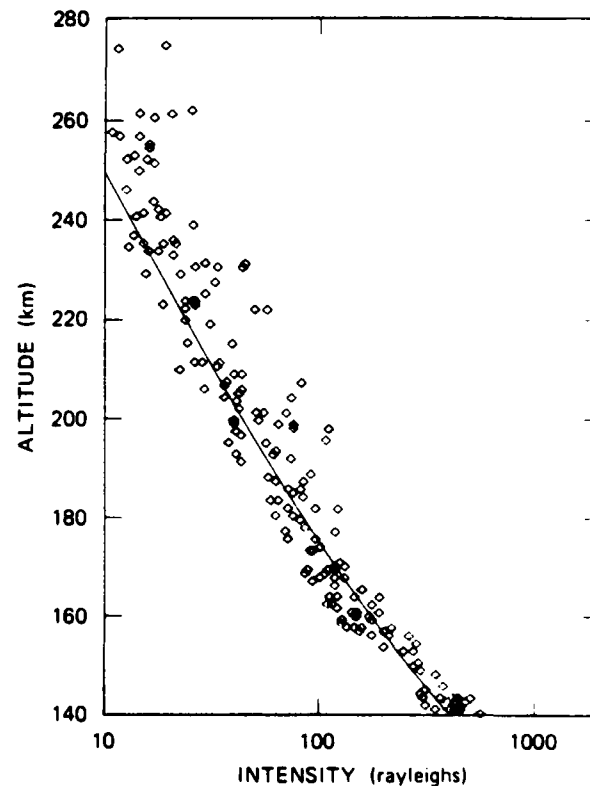Fig. 1. Comparison of Yee and Abreu (1982) 6563 Å intensity vs altitude data, and $O(^3P)$-O_2 model.

tive as the former. It is interesting to note the thermodynamic equivalence of 5 eV $O(^3P)$ and 10 eV O_2, since the O_2 bond strength is 5 eV.

The shape of the 7320 A data is the same as that taken at 6563 A over all but the lowest 10 km of the 140-280 km range. It would be extremely interesting to make measurements down to 120-130 km, in order to be certain that there is really an increasing I(7320)/I(6563) ratio below 150 km, perhaps a consequence of an additional emission feature at the longer wavelength. However, it is precisely the low altitude 7320 A data that Yee and Abreu analyzed to extract the 5 ms lifetime which we have attributed to OH.

It is useful to make a radiative efficiency calculation, which indicates that only a small fraction of the collisions between surface and particles results in production of a photon. We take 190 km as a reference altitude, where $[O(^3P)] = 4 \times 10^9$ cm^{-3}. At a velocity of 8×10^5 cm s^{-1}, the $O(^3P)$ flux is 3.2×10^{15} atoms cm^{-1} sec^{-1}. With the 20 A bandwidth 7320 A filter, approximately 5% of the 8-3 band can be detected. The 8-3 band represents 0.2% of the emission from OH(v = 8) [Mies, 1974], and the v = 8 level represents 30% of the initial distribution of vibrational levels in OH, according to our H + O_3 reaction model (Streit and Johnson, 1976). Thus, the filter detects 3×10^{-5} of the OH produced. At 190 km, the detected intensity is 100 R, which, as a surface brightness, corresponds to 1×10^8 hv cm^{-2} s^{-1}. Dividing by 3×10^{-5} gives an OH production rate of 3×10^{12} OH cm^{-2} s^{-1}, just 0.1% of the $O(^3P)$ flux. As the process under discussion has not yet been demonstrated to be a source of vibrationally excited OH, it is encouraging that it is not required to be highly efficient.

To calculate the total radiation, we need to include the fact that all the OH vibrational energy is lost by radiation, i.e. v = 8+6+4+2+1+0 is the main sequence from v = 8. Thus, each v = 8 molecule radiates its total energy, 3.2 eV. The radiative energy is then 6.4×10^{12} eV cm^{-2}s^{-1} or 1 µw cm^{-2}, produced principally at 1-2 µm. At lower altitudes, the Yee and Abreu data indicate that this figure exceeds 10 µw cm^{-2}.

In summary, it has been shown that the OH Meinel bands are a tenable identification for the AE satellite and space shuttle glows. The behavior of the intensity as a function of the altitude is consistent with a model in which OH is ejected from the surface by both 5 eV $O(^3P)$ atoms and 10 eV O_2 molecules, with the latter being four times more effective. The lifetime of the emitter as calculated by Yee and Abreu is in excellent agreement with the OH radiative lifetimes, and the spectral distribution based on the two wavelengths they measured is as expected for highly vibrationally excited OH. The necessary efficiency for the conversion of 5 eV $O(^3P)$ to OH is only 10^{-3}. Finally, the spectral cut-off as observed on the space shuttle is also consistent with OH Meinel bands.

On the negative side, Torr et al. (1977) in their initial observations of this phenomenon,

claimed that a similar effect existed at all wavelengths that they measured, between 3371 and 7319 A. This is of course inconsistent with the space shuttle observations, where the glow is definitely orange-red. However, Yee and Abreu (1983) have now quantified the photometric intensities, and it is apparent that the blue and uv radiation is much weaker than that in the red (and could in principle be the originally surmised emission from recombining oxygen atoms). The 10 meter glow region deduced from Yee and Abreu's calculations is certainly much larger than shown in the space shuttle photographs; a photograph of the satellite would give a more direct comparison. The ultimate analysis of these glows will eventually come from spectroscopic measurements.

References

Ackerman, M., P. Simon, U. von Zahn, and U. Laux, "Simultaneous Upper Air Composition Measurements by Means of UV Monochromators and Mass Spectrometers," J. Geophys. Res. 79, 4757 (1974).
Aviation Week and Space Technology, "Orbiter Glow in Dark Concerns NASA," 116, 14 (1982).
Banks, P. M., private communication (1982).
Banks, P. M., P. R. Williamson, and W. J. Raitt, "Observations of Vehicle Glow on STS-3," Geophys. Res. Lett. (this issue, 1983).
Broadfoot, A. L. and K. R. Kendall, "The Airglow Spectrum, 3100-10,000 A," J. Geophys. Res. 73, 426 (1968).
Harteck, P. and R. R. Reeves, Jr., "Formation and Reaction of the Excited $O_2(A^3\Sigma_u^+)$ Molecules," Disc. Faraday Soc. 37, 82 (1964).
Jacchia, L. G. "Revised Static Models of the Thermosphere and Exosphere with Empirical Temperature Profiles," Smithsonian Astrophysical Observatory, Special Report 332 (1971).
Mies, F. H. "Calculated Vibrational Transition Probabilities of OH($X^2\Pi$)", J. Molec. Spectrosc. 53, 150 (1974).
Streit, G. E. and H. S. Johnston, "Reactions and Quenching of Vibrationally Excited Hydroxyl Radicals," J. Chem. Phys. 64, 95 (1976).
Torr, M. R., P. B. Hays, B. C. Kennedy, and J.C.G. Walker, "Intercalibration of Airglow Observations with the Atmosphere Explorer Satellites," Planetary Space Sci. 25, 173 (1977).
Yee, J. H. and V. J. Abreu, "Optical Contamination on the Atmosphere Explorer-E Satellite," SPIE Proceedings, Vol. 338, (1982).
Yee, J. H. and V. J. Abreu, "Visible Glow induced by Spacecraft-Environment Interaction," Geophys. Res. Lett. (this issue, 1983).

APPENDIX B

DEDUCTIONS FROM SPACE SHUTTLE GLOW PHOTOGRAPHS

T. G. Slanger

Chemical Physics Laboratory, SRI International, Menlo Park, CA 94025

DEDUCTIONS FROM SPACE SHUTTLE GLOW PHOTOGRAPHS

T. G. Slanger

Chemical Physics Laboratory, SRI International, Menlo Park, CA 94025

Abstract. It is shown that from the appearance of certain photographs taken from STS-5, it is possible to make several useful statements about the production mechanism of the visible glow around the shuttle, and presumably other space vehicles. These are: 1) the electronic excitation of particles in the gas phase by either electrons or fast neutrals is probably not important, 2) the interaction of thermal atoms and molecules with the surfaces does not generate the glow, and 3) translational energy accommodation of fast particles is efficient enough that a single surface collision reduces the kinetic energy below the threshold for glow production. There is no glow without the direct interaction of fast particles with the surfaces, and the sum of the contributions of the three above processes does not exceed 14% of the observed surface intensity.

Discussion

It is by now well known that spacecraft glow occurs only on surfaces facing the direction of motion of the vehicles (the ram direction) [Yee and Abreu, 1983; Mende, et al. 1984]. Since it has been demonstrated that the particle density is higher than ambient by at least two orders of magnitude near forward-facing surfaces [Murphy, et al. 1983], one may initially conclude that either emission is generated only at surfaces struck by the incoming fast particles, or that it is only produced in regions where the density is relatively high.

A point that has not been discussed in the literature is that there are conditions under which these two effects are separable, that is, photographs exist that show regions of high pressure which are not struck by fast particles. Figure 1 is taken from Mende, et al. (1984), and shows image-intensified photographs, taken from the aft flight deck window, of the vertical stabilizer and port rocket pod of the shuttle. The particles are impinging on the surfaces with the direction of motion shown, and the critical point is that in Figure 1b there is a V-shaped region between the tail and the pod. The left side of the V has its surface 30 degrees from the direction of the particle flux, and shows strong emission, while the right side of the V, with its surface

parallel to the particle flux, shows no trace of emission. It is important to note that the rocket pod and the tail are attached to each other, so that the V is real and not an optical effect. Since the glow on the tail reaches the bottom of the V, the non-glowing surface is not shadowed, and as glows have been detected at angles very close to 90° [Mende and Swenson, 1985], the appearance of Figure 1b is quite consistent with the particle flux being parallel to the non-glowing surface.

On other photographs where the tail is parallel to the ram direction, it can be argued that the density at the surface is not far from ambient, but in Figure 1b there is a non-glowing surface where the density is clearly the same as it is near the adjacent glowing region. It therefore follows that no hypothesis that suggests that the glow mechanism involves gas phase excitation can be valid, since the region above the non-glowing surface is bombarded by incoming atmospheric particles, by particles ejected from the nearby tail surface, and by any charged particles that may be generated.

Recent calculations [Hueser and Brock, 1985; Rantanen, et al. 1985] of the relationship between density and distance from spacecraft surfaces are consistent with observations, indicating pressures above ambient by about two orders of magnitude at shuttle orbital altitudes. On this basis, it has been suggested that gas phase processes, at densities of 10^{11}-10^{12} cm^{-3}, may be responsible for the glow [Rantanen, et al. 1985; Green, et al. 1985]. This possibility appears to be ruled out by the situation exemplified in Figure 1b, at least for the pertinent altitude, 305 km. At lower altitudes, for example below 160 km, where Yee and Abreu (1983) have reported that glow intensities observed from the Atmosphere Explorer satellite are no longer proportional to the oxygen atom density, gas phase processes may play a role.

An hypothesis has been put forth by Papadopoulos (1984) that spacecraft glow is at least in part a plasma phenomenon, and that electric and magnetic fields develop close to the surfaces, which ultimately result in acceleration of electrons to tens of eV, and at these energies, the particles that have been swept up by the vehicle can be excited, and are the source of the glow. Thus, the hypothesis requires that there be a substantial overpressure on the front surfaces, as found. However, to explain the observation in Figure 1b, where the densities near the apex are certainly comparable on both sides of the V, it then becomes necessary to postulate that the charged particles are only to be found on

(a)

80 deg

(b)

30 deg

(c)

-97 deg

c. Ram angle -97°

Fig. 1. Shuttle Glow on Tail Section,
Mission STS-5, Altitude - 305 km

the left side and not on the right side. It
is difficult to give credence to such an
idea, particularly since it is so evident
that, at constant density, it is the
inclination of the surface to the ram
direction that is the critical issue.
Although there may be a component of the
glow that is plasma-related, it would appear
to be minor.

It has been argued many times that the
high velocity of the shuttle, with its
resultant high impact energy of atmospheric
particles, is the primary source of space-
craft glow. Since the particle energies are
invariant, velocities always being 7.5-7.9 x
10^5 cm/s in circular low earth orbit, it is
not possible to determine the process
thresholds. From Figure 1b, we can at least
say that particles at thermal energies do

not give the glow. This is based on the
supposition that the composition of the
atmosphere collected by the vehicle's for-
ward surfaces is expected to be not very
different from ambient, i.e. 90% oxygen
atoms and 10% N_2 at 305 km, the orbiting
altitude of STS-5. Shuttle tiles (basically
SiO_2) should be inefficient surfaces for
oxygen atom recombination. With only some
metals and metal oxides as exceptions, 0
atom surface recombination coefficients are
in the 10^{-3} - 10^{-5} range [Greaves and
Linnett, 1959; Kaufman, 1961] so a large
fraction of the atoms impinging on the
spacecraft will diffuse away from it without
recombining. It therefore follows that the
thermalized oxygen atoms collected in the V
are ineffective in causing shuttle glow,
implying that the translational energy of
the atoms (or molecules) is in fact required
in the glow-generating process, although
nothing can be said about the threshold.
The absence of glow on the inside surface of
the pod in Figure 1b is also an indication
that translational energy accommodation is
fairly complete, or at least that particles
bouncing off the glowing surfaces have
retained insufficient energy to generate
glow on the right side of the V.

The suggestion has been made that the
role of translational energy in the incoming
particles may be to prepare surface sites
for processes that subsequently take place
at thermal energies [Kofsky and Barrett,
1985]. Conceivably such a conditioning
process could be operative on spacecraft,
but difficult to observe in the
laboratory. However, Figure 1b makes such
an hypothesis somewhat questionable. The
non-glowing surface had been glowing two
minutes prior to the taking of the picture,
as shown in Figure 1a, while the shuttle
slowly rotated about its principal axis at
25° per min. Furthermore, since in Figure
1a there is a bright glow on the tail when
it is within 10° of being parallel to the
ram direction, one may conclude that the
interior pod surface was glowing within 24 s
of the taking of the picture in Figure 1b.
Since there is no discernible glow on that
surface, it seems that the "deconditioning
lifetime" must be on the order of 10 s or
less. As a monolayer consists of 10^{15} atoms
cm^{-2}, a flux of surface deconditioner of at
least 10^{14} particles cm^{-2} s^{-1} is required
for complete coverage. Surface migration to
active sites may make the necessary decondi-
tioning flux considerably smaller than this,
but it is difficult to imagine any gas
phase-surface interaction proceeding at even
1% of this value (it is assumed that the
ambient $O(^3P)$-N_2 atmosphere does not con-
tribute to surface poisoning). On the other
hand, if surface deactivants arise from
upwelling of material from the interior of
the tiles, which have a very large absorp-
tive capacity, then it is not possible to
disprove the concept of site preparation
without further testing. It should be
pointed out that Banks, et al. (1983)
reported that there was no evidence for a
time delay in glow extinction on STS-3 as

shuttle surfaces rotated out of ram, but the rate of rotation (8°/min) was so slow that our deconditioning lifetime estimate can not thereby be decreased.

Finally, one may obtain a value for the extent of the glow from Figure 1b. Detailed calculations have been made by both Yee and Dalgarno (1983) and by Mende and Swenson (1985), indicating an e-folding distance from the tail glow of 20 cm, the complexity in the analysis being the fact that the line of sight is not parallel to the surface. Thus, part of the apparent thickness is just due to the fact that the flat portion of the tail itself is being observed. When the glow is weak or unamplified, as in the earliest shuttle photographs [Banks, et al. 1983], it does not appear to extend beyond the surface at all; this is a geometric and film sensitivity effect.

By the simple expedient of overlaying a photograph of the tail and pod structure, seen in reflected light (Figure 1c), over the photograph showing the glow, an estimate of the thickness can be made. The dotted line in Figure 1b shows the outline of the structural features, and the excess thickness gives the extent of the glow. The distance from the tail mid-line to the top of the rocket pod is 2.2 meters, giving a glow thickness of 40 cm. This is of course not an e-fold distance, but the maximum distance over which glow can be observed with this particular optical arrangement. For a 20 cm e-fold distance, the intensity at 40 cm is less than the surface intensity by a factor of 7. This is a reasonable film dynamic range, and suggests that there is little problem with film blooming or scattering of light in the optical elements of the recording system.

The factor of 7 thereby defines the term "lack of emission" as it pertains to the right side of the V in Figure 1b. The undiscerned emission on the apparently nonglowing part of the V could have an intensity as great as 14% of the surface intensity on the vertical stabilizer. This means that it cannot at present be disproved that the various suggested glow sources that we have discussed and set aside do not contribute, up to this limit, to the overall intensity.

Summary

Although there is still considerable controversy about the emitters(s) causing spacecraft glow, we deduce from existing photographs of the shuttle glow on tile surfaces that it is not a plasma phenomena, that it does not involve gas phase excitation, that it does not take place with thermalized particles, that there is some doubt that surface conditioning by fast particles can be important, and that direct interaction of fast particles with surfaces is the primary source of the emitting species.

References

Banks, P. M., P. R. Williamson, and W. J. Raitt, Space Shuttle Glow Observations, Geophys. Res. Lett., 10, 118, 1983

Greaves, J. C. and J. W. Linnett, Recombination of Atoms at Surfaces, Trans. Faraday Soc., 55, 1346, 1959.

Green, B. D., W. J. Marinelli, and W. T. Rawlins, Spectral Identification/Elimination of Molecular Species in Spacecraft Glow, 1985. Second Workshop on Spacecraft Glow, NASA Conference Publication 2391, Huntsville, Alabama, May 6-7, 1985

Hueser, J. E. and F. J. Brock, Shuttle Vertical Fin Flowfield by the Direct Simulation Monte Carlo Method, 1985. Second Workshop on Spacecraft Glow, NASA Conference Publication 2391, Huntsville, Alabama, May 6-7, 1985

Kaufman, F., Reactions of Oxygen Atoms, Progress in Reaction Kinetics, Vol. 1, G. Porter, ed., Pergamon Press, 1961.

Kofsky, I. L. and J. L. Barrett, Surface-Catalyzed Recombination into Excited Electronic, Vibrational, Rotational, and Kinetic Energy States: A Review, 1985. Second Workshop on Spacecraft Glow, NASA Conference Publication 2391, Huntsville, Alabama, May 6-7, 1985

Mende, S. B. and G. R. Swenson, Vehicle Glow Measurements on the Space Shuttle, 1985. Second Workshop on Spacecraft Glow, NASA Conference Publication 2391, Huntsville, Alabama, May 6-7, 1985

Mende, S. B., R. Nobles, P. M. Banks, O. K. Garriott, and J. Hoffman, Measurement of Vehicle Glow on the Space Shuttle, J. Spacecraft, 21, 374, 1984

Murphy, G. B., S. D. Shawhan, and J. S. Pickett, Perturbations to the Plasma Environment Induced by the Orbiter's Maneuvering Thrusters, 1983. AIAA Shuttle Environment and Operations Meeting, Washington D.C., October 31 - November 2, 1983

Papadopoulos, K., On the Shuttle Glow (the plasma alternative), Radio Science, 19, 571, 1984

Rantanen, R., R. Swanson, and D. Torr, A Mechanism for the Local Concentration Enhancement of the Shuttle Atmosphere, 1985. Second Workshop on Spacecraft Glow, NASA Conference Publication 2391, Huntsville, Alabama, May 6-7, 1985

Yee, J. H. and V. J. Abreu, Visible Glow Induced by Spacecraft-Environment Interaction, Geophys. Res. Lett., 10, 126, 1983

Yee, J. H. and A. Dalgarno, Radiative Lifetime Analysis of the Shuttle Optical Glow, 1983. AIAA Shuttle Environment and Operations Meeting, Washington D.C. October 31 - November 2, 1983

APPENDIX C

Articles Published and in Preparation
Resulting from AFOSR Support

1. T. G. Slanger, "Conjectures on the Origin of the Surface Glow of Space Vehicles," Geophys. Res. Lett. 10, 130 (1983). (Appendix A of this report).

2. T. G. Slanger, "Deductions from Space Shuttle Glow Photographs," Geophys. Res. Lett. 13, 431 (1986). (Appendix B of this report).

3. R. L. Sharpless and T. G. Slanger, "Oxygen Atom Recombination into Electronically Excited States on Metallic Surfaces," in preparation, to be submitted to J. Chem. Phys.

4. R. L. Sharpless and T. G. Slanger, "Temperature Dependence of $O_2(a^1\Delta_g)$ Destruction on Metallic Surfaces", in preparation, to be submitted to J. Chem. Phys.

Invited Talks Given on Research Topics Supported by AFOSR

1. Presentation at JASON meeting in San Diego, CA, on Space Shuttle Glow, (1984).

2. Gaseous Electronics Conference, Monterey, CA (Oct. 1985): "The Space Shuttle Glow".

3. 69th Canadian Chemical Conference, Saskatoon, Saskatchewan, Canada (June 1986): "Some Interpretations of Spacecraft Glow Observations".

END

10 86

DTIC